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STUDIES ON THE HYDROGENATION OF LINSEED OIL
IN RELATION TO FLAVOUR REVERSION

A thesis submitted to
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by

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TABLE OF CONTENTS

I. GENERAL INTRODUCTION

II. HISTORICAL INTRODUCTION

<u>A. Hydrogenation</u>	2
1. General	2
2. Processing a Vegetable Oil to Produce an Edible Shortening	4
3. Changes Which Occur During Hydrogenation	11
4. Reaction Rate	17
5. Conjugated Hydrogenation	19
6. Other Means of Hardening Edible Oils	20
<u>B. Flavour Reversion</u>	21
1. General	21
2. Causes of Reversion	22
3. Prevention of Reversion	26
4. Judgment of Flavours and Odours	27

III. METHODS

<u>A. Refining</u>	29
1. Alkali Refining	29
2. Bisulphite Refining	29
3. Adsorbent Refining	30
<u>B. Preparation of Catalysts</u>	31
<u>C. Hydrogenation</u>	32
1. The Apparatus	32
2. Operation	34
3. Adjustment of Temperature	36

4. Calibration	37
5. Rate of Reaction	42
D. <u>Deodorization</u>	44
E. <u>Analytical Procedures</u>	47
1. Acid Value	47
2. Iodine Number	47
3. Peroxide Content	50
F. <u>Conjugated Hydrogenation</u>	50
G. <u>Judgment of Quality of Shortening</u>	52
1. Quantitative Estimate by Panels	52
2. Flavour Judgment by Panels	54
3. Odour Judgment by Panels	55
4. Qualitative Judgments	55
H. <u>Addition of Antioxidants</u>	56
IV. EXPERIMENTAL	
A. <u>Modifications of Established Practice</u>	58
1. Effect of Catalyst Concentration	58
2. Hydrogenation at Different Temperatures	64
3. A Study of Refining Procedures	68
4. The Effect of Degree of Hardening	71
5. Blending Linseed Oil Shortening with Sunflower Seed Oil	72
6. A study of Different Samples of Linseed Oil with Different Treatments	75
7. Recovery of Catalyst	85
8. Conjugated Hydrogenation	86
B. <u>Causes of Reversion and the Use of Special Techniques</u>	88

1. The Saponifiable and Unsaponifiable Fractions	88
2. Free Fatty Acids	91
3. Linolenic Acid	93
4. Isomerization	96
5. Effect of Oxidation	97
6. The Relation of Oxidation to Reversion	98
7. Fractionation with Acetone	106
8. The Use of Antioxidants	113

V. DISCUSSION OF RESULTS

A. <u>The Hydrogenation Reaction</u>	127
1. The Catalyst	127
2. The Reaction Rate	127
3. Conjugated Hydrogenation	129
4. Hardening by Isomerization	130
5. Recovery of Catalyst	130
B. <u>Flavour Reversion Studies</u>	131
1. Judgment of Quality	131
2. Modifications in Processing	132
3. Causes of Reversion	134

VI. SUMMARY

VII. CLAIMS TO ORIGINAL RESEARCH

VIII. BIBLIOGRAPHY

LIST OF TABLES

Table No.

I. Analysis of flavour judgments: (a) muffins	82
II. Analysis of flavour judgments: (b) biscuits	83
III. Analysis of flavour judgments: (c) pastry	84
IV. Efficiency of recovered catalysts	86
V. Acid value at different stages in processing	92
VI. Test of judges on panel	99
VII. Relation of peroxide content to reverted odour	101
VIII. Acetone-crystallized fractions	109
IX. Formula C added in processing	114
X. Formula C at different levels	115
XI. Glycerol gallate (with addenda)	118
XII. Formula C with isopropyl gallate	125

LIST OF FIGURES

Figure No.

1. Hydrogenation apparatus	33
2. Calibration curve (charge vs. volume correction)	40
3. Calibration curve (volume factor vs. iodine number)	43
4. Deodorization apparatus	45
5. Conjugated hydrogenation apparatus	51
6. Hydrogenation curves: refined oil (conc. vs. time)	59
6'. Hydrogenation curves: refined oil (log. conc. vs. time)	60
7. Hydrogenation curves: crude oil (conc. vs. time)	61
7'. Hydrogenation curves: crude oil (log. conc. vs. time)	62
8. Catalyst efficiency curve	63a
9. Hydrogenation curves: refined oil (conc. vs. time)	65
10. Hydrogenation curves: refined oil (conc. vs. time)	66
10'. Hydrogenation curves: refined oil (log. conc. vs. time)	67
11. Temperature efficiency curve	69
12. Flavour judgments: different oils (a) muffins	79
13. Flavour judgments: different oils (b) biscuits	80
14. Flavour judgments: different oils (c) pastry	81
15. Conjugated hydrogenation curve	87
16. Hydrogenation curve: free fatty acids	94
17. Development of peroxides and odour: Sample (1)	104
18. Development of peroxides and odour: Sample (2)	105
19. Development of peroxides and odour: Linolenic acid	107
20. Acetone fractions: Sample (1) (peroxide and odour vs. time)	110

21. Acetone fractions: Sample (2) (peroxide and odour vs. time)	111
22. Acetone fractions: Sample (3) (peroxide and odour vs. time)	112
23. Formula C in processing (peroxide vs. time)	116
24. Formula C in processing (odour vs. time)	117
25. Formula C at different levels (peroxide vs. time)	119
26. Formula C at different levels (odour vs. time)	120
27. Glycerol gallate (peroxide vs. time).	121
28. Glycerol gallate (odour vs. time)	122

I. GENERAL INTRODUCTION

The shortage of edible fats and oils in Canada following the outbreak of war became critical during the latter part of 1942 and early 1943. Since linseed oil is the only vegetable oil produced in appreciable quantities in Canada, this study was projected to investigate the possibility of utilizing it in the manufacture of an edible shortening. Complete hydrogenation to a stearin would allow the use of small proportions in blending with low-melting fats, but could provide only for the use of very limited amounts. Attempts to use a partially hydrogenated linseed oil (having suitable physical properties for a shortening) showed that there was a serious problem involved, for products baked with this shortening had an unpleasant flavour and odour.

In the study of this problem it was sought first to learn, as soon as possible, whether through a modification of the techniques at present used in the industry, it might be possible to produce a more acceptable shortening. Thus modifications in the customary processing steps were investigated. Following this, certain more fundamental aspects of the flavour reversion problem and certain special treatments of the oil were studied. The immediate problem has been that of producing an edible product, and to some extent the urgency of this side of the investigation has restricted the opportunities for more fundamental studies.

II. HISTORICAL INTRODUCTION

A. HYDROGENATION

1. General

It was long ago realized that the supply of naturally hard fats was inadequate to supply the needs for making soap, etc., and for edible purposes. The use of the much more abundant and relatively cheap liquid oils for these purposes was made possible through hardening them by hydrogenation. Credit for showing how this might be done efficiently and economically is generally given to Normann who received a British patent in 1903 (89). This patent had disclosed that the unsaturated fatty acids or their glycerides might be converted into saturated compounds by treatment in the liquid state with hydrogen in the presence of a finely divided metal such as platinum, iron, cobalt, copper and especially nickel, adapted to act as a catalyst. The process was very rapidly put on an industrial basis for soap-making and somewhat less quickly for the production of edible products.

Interest at first was limited to converting a liquid to a solid fat in the quickest and cheapest way. Consideration was given principally to design of equipment, development of efficient catalysts, techniques for removal of catalyst and studies on the various catalyst poisons that had to be avoided. Then, for the edible industry, came a critical period during which studies were made on the digestibility of hardened fats as well as the possible harmful effects of small

amounts of nickel. Clayton (27 p.26) states that by 1920 it was generally agreed that nickel in the amounts likely to be present in hardened oils had no detrimental physiological action and that these hardened fats had equally as high digestibility as natural fats.

When these problems had been thus satisfactorily answered the oil-hardening industry could feel secure. It could no longer be doubted that it was an industry which was here to stay. At this point investigations turned to studies on the mechanism of the reaction, and in the edible industries to increasing resistance to rancidity, and to improving physical properties at various temperatures. Studies on the changes in the fatty acids during hydrogenation complicated greatly the simple picture originally held of hydrogen adding at a double bond to bring saturation. First, a selective feature was noticed about this addition, and secondly, iso-acids were noticed among the products making analyses more difficult and the complete picture less clear.

The present discussion will deal with the hardening of a vegetable oil to produce an edible shortening. First the customary processing steps will be dealt with in order. Then the basic step of hydrogenation will be considered as to the changes which occur during the reaction and the rate of the reaction. Finally, mention will be made of conjugated hydrogenation and hardening by elaidinization.

Acknowledgment is made to a number of references which have been helpful in preparing various sections of this review (34 pp.1-417, 52 pp.202-25, 75, 84, 131).

2. Processing a Vegetable Oil to Produce an Edible Shortening

The complete process which must be carried out in industry consists of a number of individual processes or steps. These will be considered separately.

a. Refining the crude oil

This is considered very important since such substances as free fatty acids, albuminous matter, organic sulphur compounds, traces of phosphorus-containing lecithin, etc., all interfere with the hardening process through exercising a toxic effect on the catalyst.

The normal refining process employs alkali refining and adsorbent bleaching to prepare an oil for hydrogenation.

There may often be actually four operations involved:

- (1) Pretreatment or desliming. This may consist only of settling or filtering with diatomaceous earth. However it may involve a treatment with water, steam, or even mineral acids.
- (2) Neutralizing. This is generally carried out using a sodium hydroxide solution with concentrations, temperatures and times varying with different oils and different plants. Conditions of stirring, etc., must be such as to give good mixing but without formation of emulsions. Soaps formed should agglomerate so as to settle quickly. The content of free fatty acids is reduced to about 0.04 per cent. Continuous processes have been introduced which depend on a centrifugal separation of the foots. These are suitable when one oil of approximately constant composition is treated.

(3) Washing. This step is included to remove the last traces of soap, and since in industry it is important to have a small loss in alkali refining, it is preferred to wash out any excess of alkali rather than allow it to be used up in saponifying some of the oil. Washing may be accomplished with water alone or may include the use of a solution of sodium chloride; the last traces of moisture may be removed by vacuum drying.

(4) Bleaching. This is generally carried out by agitating the oil at a specific temperature with a definite amount of some adsorbent substance such as fuller's earth, or activated charcoal. Separation is then effected by filtering.

b. Production of hydrogen

In addition to the oil which is to be hydrogenated, two other materials must be supplied: hydrogen and the catalyst. For the purposes of this review we need not discuss at length the methods used in the preparation of the hydrogen. It is sufficient to say that the electrolysis of water gives the purest hydrogen. However, consumption of electric power is high and unless this is cheap the users of hydrogen are obliged to look to other means of production.

c. Production of catalyst

In the preparation of a catalyst many metals and metallic compounds have been suggested, but metallic nickel is the most satisfactory from an economical and industrial point of view. Whitner (131) states that the following may also be used as metals and in some cases as oxides: platinum, palladium,

iridium, rhodium, ruthenium and osmium. These catalysts appear to possess the property of bringing about hydrogenation at temperatures considerably lower than those required for nickel. Their greater activity is however insufficient to balance the much greater cost. Cobalt and copper also display certain hydrogenating activity but are not so widely applicable as nickel.

Nickel in the form of a smooth metallic surface, e.g., metal turnings or electrolytically deposited films, has no catalytic activity. It must be specially prepared to have the active centres which are required to bring about a reaction. Four distinct methods of preparation are in common use.

(1) Dry method. A carefully precipitated, washed and dried nickel carbonate or hydroxide is reduced in a current of hydrogen gas at temperatures varying from 300-500°C. The active nickel may or may not have an inert substance as carrier. If it is desired to use a carrier, the inert material (generally kieselguhr) is added to a solution of the nickel (sulphate or nitrate) and the nickel carbonate or hydroxide is precipitated on the carrier. This is then washed, dried, and reduced. In the majority of cases it is preferred to have the nickel mounted on such a support. This serves to spread the nickel so that a greater surface is available for catalysis and also provides a material which can be washed more readily to purify it prior to reduction and which can be more readily filtered from the oil at the conclusion of hydrogenation. The finally prepared catalyst is pyrophoric

in nature and must be protected from air, either by keeping it in an atmosphere of carbon dioxide or in an oil or fat medium. Bag (10) suggests that it is sufficient for the catalyst to be cooled in an atmosphere of carbon dioxide gas; it may then be kept for one month in air without loss of activity. The dry method has found considerable use especially for laboratory studies. For industrial use it is less favored because it is slow and costly, and the product lacks uniformity.

(2) Wet method. An easily decomposable nickel compound, such as nickel formate, is suspended in an oil and is reduced in an atmosphere of hydrogen at a temperature of 200-250°C. for 2 to 4 hours.



This leaves a finely dispersed catalyst which has high activity and is quite uniform.

(3) Alloys. An alloy of nickel with silicon or aluminium is treated with an aqueous solution of sodium hydroxide. This dissolves the silicon or aluminium and leaves a finely divided nickel.

(4) Massive. Turnings or small pieces of nickel are placed in a long perforated cylinder having a nickel rod through the centre of the mass, which serves as an electrode. The small masses are subjected to anodic oxidation so as to become coated with a film of oxide; then, while hot oil and hydrogen pass through, the oxide is reduced to furnish a surface of active metal. This type is most useful in preparing the

catalyst for the continuous process of hydrogenation(74).

(d) Hydrogenation of the oil

The usual hydrogenation process is a liquid-phase operation in which hydrogen is intimately mixed with the heated oil in contact with finely divided catalyst. Temperatures of 175-200°C. are generally used but the reaction has been reported as taking place at 50°C. (135) and at 300°C. (114). The hydrogen pressure is generally one atmosphere or slightly higher although the reaction has been carried out at reduced pressures, e.g., 20mm. (Excourrou, 38) and at pressures of 195 atmosphere and above (Waterman and Van Dijk, 125). Within limits, and increase in pressure will reduce the temperature required. However, pressures near atmospheric are preferred in industry since it is difficult to prevent loss of gas by leakage at high pressures.

Two distinct methods are employed to secure intimate contact of oil, catalyst and hydrogen:

(1) The batch process. Hydrogen is passed through the hot, well-agitated oil in the presence of a powdered catalyst. This may be carried out in two ways:

(a) The Normann process. The hydrogen is conducted into a vigorously agitated mixture of oil and catalyst.

(b) The Wilbuschewitch process. The mixed oil and catalyst are sprayed in at the top of a hydrogen-filled chamber. The mixture may be withdrawn and sprayed in any number of times to get the desired amount of hardening.

(2) The continuous process (Bolton and Lush, 74,77). The hot oil and hydrogen are passed over a special stationary catalyst. This also has been carried out in two ways:

(a) The drip method. The oil flows downward over the catalyst to meet an upward current of hydrogen..

(b) The overflow method. The catalyst chamber is filled with oil which is made to overflow from vessel to vessel.

Although the continuous process would appear to be particularly advantageous, and working models have demonstrated its feasibility; this type of hydrogenation is remarkably unselective (a feature which will be discussed later). This factor has prevented it from being widely accepted. Thus the present technically important processes of hydrogenation are of the batch type and these will be considered almost exclusively in the present discussion.

In laboratory studies the hydrogenation apparatus is usually made of glass and equipped with an external oscillating shaker or with a paddle stirring device. Constant temperature is maintained by an external electric heating coil with asbestos wrapping for insulation, or by immersing the apparatus in an oil bath. Provision may be made for withdrawing small samples for analysis. The catalyst most commonly used is reduced nickel carbonate on a kieselguhr support. It is added either directly in the flask or diluted with an inert solvent which may easily be removed. The hydrogen is measured by a pressure gauge or by a flow meter. The course of the hydrogenation is followed by observing the

decrease in refractive index of samples taken at intervals, or by checking the volume of hydrogen absorbed. Iodine number determinations on a series of samples cannot be made quickly enough to keep pace with the reaction, but this may serve as an accurate means of plotting the course of a reaction after it has been completed. After hydrogenation (even by the continuous process) the oil must be filtered while at a temperature of 60-70°C. to remove the catalyst.

(e) Deodorization

This process effects the removal of inherent odours and flavours as well as a characteristic hydrogenation odour. It is a highly specialized type of steam distillation carried out at temperatures of 175 to 220°C. and under a pressure of not more than 3 or 4 cm. and commonly less than one cm. However one worker has suggested (7) that a pressure of 2.5 cm. is preferable to 0.6 cm. since a greater weight of steam may be taken through and the deodorization time thereby reduced. The volatile substances removed may be terpenes, ketones, alcohols, acids or aldehydes in the majority of vegetable oils. It is important at the end of this treatment, while the fat is hot, to prevent inclusion of air. It may also be necessary to filter the fat again.

(f) Catalyst recovery

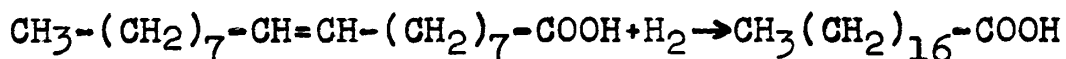
This is important in large plants; in smaller ones it may not be economical and then the spent catalyst is sold to manufacturers of nickel salts. Loss of catalyst activity is

attributed (3) to two factors which decrease the hydrogen pressure at the catalyst surface, i.e., (1) presence of poisons (especially sulphur, also halogens, arsenic or phosphorus) and (2) preferential adsorption of gaseous impurities at the surface. Reactivation may be effected by washing off excess fat with a solvent as petroleum ether, diethyl ether, or carbon tetrachloride, heating in a furnace to remove oxidizable and volatile impurities, and finally reduction again to metallic nickel. If this is not effective, it is necessary to dissolve the nickel in acid (41,111) and from the purified solution, prepare the salt, e.g., carbonate, which is to be reduced, as in the original preparation of the catalyst.

3. Changes Which Occur During Hydrogenation

a. Addition of hydrogen

The fundamental change in hydrogenation is the addition of hydrogen at the double bonds of the unsaturated fatty acids. Thus oleic acid on hydrogenation is changed to stearic acid:



b. Selectivity

The oils commonly hydrogenated have both linoleic and oleic acid present and some, such as soybean oil and linseed oil, have significant amounts of linolenic acid. With these different unsaturated systems present there is an unequal competition for the hydrogen which is supplied. It has been found that the hydrogen is taken most easily and most rapidly

by the more unsaturated systems, thus there is a selective feature to the hydrogenation reaction. The more unsaturated fatty acids are reduced to less unsaturated ones before the least unsaturated are completely reduced (25). There seems to be no doubt that hydrogenation is selective but there is disagreement as to the degree of selectivity. A fairly high degree of selectivity is desirable since, for best keeping qualities, the more highly unsaturated fatty acids should be hydrogenated.

The effect of various factors on the extent of selectivity may be expressed according to Williams (132), by a figure which represents the increase in the saturated acids at the point where the unsaturated acids have been reduced to the equivalent of oleic acid. Selectivity is highest when this figure is lowest. The effect of temperature, concentration of catalyst, nature of catalyst, pressure and agitation will now be considered briefly.

Higher temperatures up to 200°C. are generally considered to favour selectivity (21,40,127,128). The numerical values, by the method of Williams, at 100 and 200°C. are respectively eleven and six. However, a decrease in selectivity has been observed at very high temperatures (31,100). Waterman and Van Vlodrop suggest that above 200°C. selection may fall off because of shifting of double bonds to conjugated positions which hydrogenate simultaneously (43). However, since hydrogenation is an exothermic reaction, it would be expected that before this happens, or in addition

to this, an increase in temperature would prevent the normal increase of rate, and cause those reactions to take place which are endothermic, namely the formation of high melting iso-acids.

Increasing catalyst concentration seems also to increase selectivity, but here the influence is much less marked (31, 99). The increase expressed by the Williams method for a five to ten-fold increase in catalyst is only one or two points. Conflicting findings have also been reported (40,87,125,128). Mitchell (84) believes that, within limits, an increase in catalyst concentration increases selectivity but at too great a concentration there is a decrease.

Nickel is a much more selective catalyst than either platinum or palladium (100,119). Thus aside from the cost there is a further good reason for the preference shown to nickel as the catalyst in industry.

Increasing pressure has the reverse effect to increasing temperature -- it causes a decrease in selectivity (87,90,119, 126). Doubling the pressure is reported to reduce the selectivity by about one half, but this is not always conceded (40,99).

Agitation also influences the selectivity of the reaction. With slow agitation there will be a longer period of contact between the oil particles and the catalyst. This will tend to cause more complete saturation of these oil particles while other oil particles, near but not in contact with the catalyst remain unchanged. Thus the reaction will be

relatively unselective. On the other hand, rapid agitation will decrease the time of contact of oil particles with catalyst thus presumably decreasing the extent to which they may become saturated. This short contact will also mean that in any time interval more oil particles will have contact with the catalyst. Thus there should be more chance of reducing all of the highly unsaturated fatty acids to a less unsaturated state before many fatty acids have been completely saturated, i.e., the reaction should be more selective.

These theoretical considerations seem to be borne out, in part at least, by the fact that in the continuous hydrogenation process where the oil flows over a stationary catalyst, mixing is obviously poor and the reaction is very non-selective (28,55,58). High-speed mixing and increased rate of hydrogen flow have shown increased selectivity, e.g., (35). However, rapid agitation will apparently bring an increase in selectivity only up to the point where the catalyst is brought into uniform suspension. Beyond this, further agitation has merely the effect of increasing the contact between oil and hydrogen which is equivalent to increasing the concentration of hydrogen and thus decreasing selectivity. In agreement with this, Waterman and Bertram (63,124) find the Normann process more selective than the Wilbuschewitch process. A contrary view has been reported by Moore, Richter and Van Arsdel (87) in finding increased agitation to be less selective.

c. Iso-acid formation

The catalytic hydrogenation of the esters of unsaturated fatty acids is often, if not always, accompanied by isomerization reactions. The isomerization will occur even in the absence of hydrogen, i.e., on heating with the catalyst alone (129,130). The term iso-oleic acid is applied loosely to include all those octadecenoic acids other than oleic, which are produced in hydrogenation. It may be concluded (12,13, 59,85,112,116,121,133,137) that it consists of a mixture of elaidic acid plus the Δ^{8-9} , Δ^{10-11} and sometimes the Δ^{11-12} , and Δ^{12-13} acids. The latter two arise from linoleic acid and the other two from oleic. There may also be elaidinization or isomerization at the double bonds in these positions.

The presence of these fatty acids gives the fat a higher melting point and in some cases advantage has been taken of this fact to employ conditions favoring their formation, thus producing a hardened fat with less hydrogen than would otherwise be required (51,86). However, there has been some difficulty in imparting the desired physical characteristics to fats of a high iso-oleic acid content so the tendency has been to favor conditions which reduce their formation. The iso-acids of hydrogenated fats have nevertheless been shown to be readily utilizable as foods, e.g., (11).

The total amount and the proportions of these acids depend on the process used and the conditions of operation. Their formation is not due to the dehydrogenation of stearic acid (112,128). There are, however, four types of change

which may occur to cause the formation of iso-acids.

- (1) Selective hydrogenation. This may cause, for example, the formation of Δ^{12-13} oleic from linoleic acid (112,137).
- (2) A bond shift toward the methyl group (14,120).
- (3) A bond shift toward the carboxyl group (121).
- (4) Cis-trans isomerism (85).

As mentioned above, the conditions of hydrogenation have an effect on the process of iso-acid formation. The effect of individual factors will be considered briefly.

Increasing the temperature is generally considered to increase the production of iso-acids (9,21,49,79,115,117). One paper (114) contradicts this, but the experiments were done at temperatures over 250°C. The reactions which give rise to the higher melting point iso-acids are endothermic, and would be expected to proceed more readily at higher temperatures.

Some workers find that the yield of iso-acids increases as the catalyst concentration is increased (9,31,79), but one investigator reports no change, probably because the temperature was over 250°C.(114). With regard to the nature of the catalyst, it is reported (85) that nickel forms less iso-acids than palladium. The method of preparing the nickel catalyst may also have a large effect (9) as may the presence of copper with the nickel(79). Increasing the pressure seems to decrease the production of iso-acids (9,118), and conversely at reduced pressures a product with a high content of iso-oleic glycerides is obtained (38,39).

Increasing the operational time is considered to favour the formation of iso-acids (49,117). The nature of the process is also reported as affecting the extent of iso-acid formation, being less in the continuous process than in the Normann process.

d. Ester interchange

Some interchange of acyl groups between the molecules of triglycerides occurs in the hydrogenation of mixtures of glycerides but the rate is comparatively slow. Atherton and Hilditch (6) find that about five per cent of the total glycerides present are involved per hour of exposure at 180°C.

4. Reaction Rate

The question of reaction rate is quite unsettled. Some report that hydrogenation proceeds normally at a constant rate at least over a large part of the reaction (2,69,99), and some find it proceeding in a step-wise manner and going at a constant rate throughout each of the two or three steps (16,22,23,74,80). Others (60,107,113) suggest that the reaction is of a first order type.

An increase in temperature is found to increase the rate (87,107) but only to a relatively small degree. The latter paper reports that the rate increases 2.8 times for a rise in temperature of 60°C. It seems probable that diffusion and the nature of the fatty acids present (4,5) may be important factors affecting the results.

Increasing the catalyst concentration is reported (40,87

and others) to bring about a corresponding increase in rate and two workers (69,75) find that doubling the concentration of catalyst increases the rate fifty per cent.

Increasing the pressure is known to increase the reaction rate, and it is generally considered that the rate is proportional to the pressure of hydrogen, however it is not agreed whether the atomic or molecular concentration should be considered. Armstrong and Hilditch (3) say it is molecular but other reported data (87,107) suggest that the rate varies with the atomic concentration, i.e., in proportion to the square root of the pressure.

The relation of agitation or speed of stirring to reaction-rate has been fully studied by Reid (61,83), and it is concluded that "in hydrogenation, a gas, a liquid, and a heavy metal powder must be brought together. With slow stirring the catalyst is probably not kept in uniform distribution and only part of it is effective. At a certain speed all of it is brought into action and from then on the rate depends on bringing the gas into contact with the liquid and the relation becomes linear."

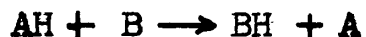
An interesting suggestion concerning the mechanism of hydrogenation has been made by two workers (2,75). They believe that an oil-catalyst complex is formed in equilibrium with the oil and catalyst, and that it is this complex alone which further reacts with the hydrogen.

Variations in hydrogenation-rate may be caused by differences in the structural arrangement of the fatty acids in

the glyceride (57,87), and the rate of hydrogenation of fatty acids alone may differ from that of the glycerides. It would appear that the presence of the free carboxyl group retards the rate of hydrogenation (56,94) but the reverse is also reported (3).

5. Conjugated Hydrogenation

This recent development in hydrogenation has received most attention from Russian workers, for example Lubarski, etc. Conjugated hydrogenation is defined as "the catalytic dehydrogenation and simultaneous hydrogenation of another substance present in the mixture at the expense of the liberated hydrogen but without its appearance in the vapor phase" (73). The reaction may be represented thus:



where AH is the substance which can be dehydrogenated and B is the unsaturated fatty acid or glyceride.

Ethyl alcohol is commonly used as the source of hydrogen. It forms acetaldehyde on losing two atoms of hydrogen per molecule. Other alcohols have also been tried in the reaction, e.g., methyl, propyl, isopropyl, isobutyl, isoamyl and hexyl alcohols (64,103) and nickel formate has served simultaneously as catalyst and source of hydrogen (1). The reaction is usually carried out by heating the oil, catalyst and alcohol in an autoclave with a nickel catalyst at about 250°C. and 30 to 40 atm. pressure (73,95). However, Bennett (17) noticed that high pressures had no advantage and

suggested that the reaction might go as well at atmospheric pressure.

The reaction is very incomplete and analyses show that the linoleic acid generally is reduced entirely, that the increase in saturated acids is small, and that oleic and iso-oleic increase by about the same amounts (103). The principal use of this process has been to produce an edible oil from sunflower seed oil which resembles olive oil in composition. This is done by chilling the oil after the conjugated hydrogenation, and then filtering to remove most of the saturated and iso-acid components (15).

6. Other Means of Hardening Edible Oils

a. Elaidinization or isomerization

This has been suggested as a means of hardening food oils to give a product which has a satisfactory colour, odour and taste. Elaidinization is combined with hydrogenation in the hardening of fish oil (96), and with conjugated hydrogenation to harden various oils (102). The commonly used catalysts are sulphur dioxide (122), selenium (18,66) and nitrogen oxides (66).

b. Hydrogenation of oxidized oils

It is reported that a white, solid hydrogenated linseed oil of superior quality is obtained by this process but it is not decided as to whether more or less hydrogen is required for this type of hydrogenation (32,105).

B. Flavour Reversion

1. General

Flavour reversion appears to be an extraordinary type of deterioration in a fat. Although it has been reported in other oils, e.g., corn and cottonseed (33), it constitutes a much more serious problem in relation to linseed and soybean oils. The term "reversion" implies the return of a flavour or odour which has at some previous time been removed, but this implication is misleading as the flavours and odours which appear in reversion are different from those which were present at any stage in processing the fat. It seems necessary to make a distinction between reversion in an oil and in hydrogenated shortening. It has been found with both linseed oil (71) and soybean oil (19), that as reversion proceeds various odours become evident. These are variously described as "grassy", "painty", "fishy", "cucumber-like", and even as resembling over-heated rubber. Such a succession of variable unpleasant odours has also been observed by the author in linseed oil. The case is different however in regard to reverted linseed oil shortening. The organoleptic sensations of taste and odour associated with such a reverted material do not resemble any of those observed in the oil, or in the hydrogenated shortening when freshly deodorized. These sensations are characteristic, and if mild may be considered pleasant, but when strong are sharp and irritating so as to be definitely unpleasant or even repulsive.

A hydrogenated and deodorized linseed oil shortening is almost free of odour and taste. It will have only that slight taste and odour which is common to vegetable shortenings. Reversion will be noticed after a few weeks storage at room temperature, 10 to 12 hours at 100°C., 1 to 3 hours at 200°C., and after as little as 8 to 10 minutes when baked in a pastry at a temperature of about 275°C.

The studies on flavour reversion which have been reported in the literature are, almost without exception, concerned with the group of "off" odours which have been observed on heating linseed or soybean oil (generally the latter). Thus, in this short review, "reversion" will have this meaning although these studies may not relate definitely to the problem of the reversion which occurs in linseed oil shortening. This topic will be reviewed first as to possible causes of reversion and second as to prevention. This will be followed by a short section on the judgment of flavours and odours.

2. Causes of Reversion

At least four sources of trouble have been suggested (19,33), viz.:

Highly unsaturated fatty acids, e.g., linolenic acid.

Oxidation products from natural antioxidants.

Nitrogen-containing substances.

Certain hydrocarbons present in small amounts.

a. Linolenic acid

The conclusion that this is in some way responsible

might be arrived at readily when it is observed that linseed oil and soybean oil contain linolenic acid, whereas none is found in sunflower seed, corn, cotton, or peanut oils. This is the most obvious difference in composition between these two groups of oils. If such were the case, the amounts present (about forty per cent in linseed oil and two to three per cent in soybean oil) would suggest that the reversion problem might be much more serious with linseed oil.

Suggestions as to the manner in which linolenic acid might behave to cause reversion have been indefinite. It has been found that the reduction of the linolenic acid component of linseed oil did not remove the flavour (98). So it would seem that if linolenic acid is the cause, it is not responsible per se, but rather in that it forms an offending product through some chemical change. Durkee (33) suggests a ring-closure mechanism or a process of ketone formation following slight oxidation. Theories which suggest an oxidation change as responsible have been held from the earliest investigations (98) and have some experimental evidence to support them (19). However, little is known of the nature of the substance oxidized, although it is implied that the unsaturated fatty acids are involved. Suggestions concerning the importance of oxidation catalysts have been made (98), including both heavy metals and organic compounds as catalysts. It was concluded though, that oxidation of the oil could proceed in the absence of these. Lemon (70) offers the suggestion that in the hydrogenation of linolenic acid the Δ^{12-13} double bond

may be saturated first to form an isomer of the common linoleic acid which, when heated, forms the odiferous product.

b. Decomposition of natural antioxidants

The second suggestion, that oxidation of the natural antioxidant present in the oil may be responsible, appears to have some theoretical basis. Reversion appears to be accelerated by the same conditions which hasten the onset of rancidity, but it may be detected before rancidity develops. The chain-theory mechanism of antioxidant function suggests that the first step in fat deterioration is the oxidation of the antioxidants present (68 p.137). This explanation of reversion appears to be inadequate since antioxidant substances in crude and in refined soybean oils have been used to stabilize other fatty materials (48).

c. Nitrogen compounds

An odoriferous nitrogen-containing substance has also been associated with flavour reversion (123). This is interesting since soybean and linseed oils still retain relatively large amounts of nitrogen (35 to 50 per cent of original) even after refining (88,108). Furthermore, nitrogen compounds are frequently responsible for unpleasant odours and flavours. Davies and co-workers (29,30) report that trimethylamine oxide is an intermediate in the production of fishiness and have associated it with the decomposition products of lecithin, choline, etc., the amount present in an oil increasing as oxidation of the fat progresses. Bickford

(19) reports that trimethylamine oxide becomes increasingly active in releasing formaldehyde, dimethyl- and trimethylamines when fatty acids of increasing unsaturation are present.

d. Hydrocarbon compounds

Saturated and unsaturated hydrocarbons having obnoxious odours have been isolated from vegetable oils and from the condensate in deodorization (19,78). These compounds have not been identified nor have they been correlated with flavour reversion.

It is evident from the above review that the problem is far from being solved. It has not been definitely established as to whether the responsible factor is in the saponifiable or in the unsaponifiable part of the oil. Broge (24) reports that herring oil lost none of its taste and odour either on removal of the unsaponifiable fraction or on separating the total fat acids, re-esterifying and refining. Davies (30) found that the unsaponifiable fraction of vegetable and animal fats does not develop an odour when heated with trimethylamine oxide although the fat acid fraction of linseed oil reduces trimethylamine oxide and acquires a fishy flavour. These findings would suggest that the flavour is probably associated with some fatty acid component of the oil interacting with certain nitrogen compounds.

3. Prevention of Reversion

a. By improved refining

Steam deodorizing and bisulphite refining reduce the formation of odour and flavour but do not prevent it(55). Bickford and co-workers (20) have studied refining techniques in relation to reversion in soybean oil and find that with more drastic alkali refining and deodorizing, the stability of the oil to reversion is reduced. By employing an improved refining technique, a marked improvement in stability has been claimed (19).

b. Antioxidants

Since the conditions retarding oxidative rancidity appear to delay the onset of reversion and since the addition of various natural and synthetic substances have been shown to have a marked effect in stabilizing fats against rancidity (46,54,91), these might be expected to exert a similar effect on reversion. An active antioxidant has been extracted from soybean meal (47) and certain polyhydroxy compounds, phosphoric acid esters of fatty acids, etc., have been found to retard flavour reversion (36,37,109).

c. Molecular distillation

Short-path distillation or molecular distillation has been claimed (109) to produce a soybean oil which did not revert. This is surprising since the oil was first freed of phosphatides and the natural antioxidants are removed in the

first fractions (44). If successful it would seem to refute any relationship of antioxidants to reversion.

d. Special refining technique

A refining technique has been used which involves rapid heating of the crude oil to the "break point", separating the reddish-brown gelatinous mass which is formed and carrying out the usual alkali-refining operation (97). It is claimed that reversion of the product is delayed or eliminated.

e. Special hydrogenation

It is reported that controlled hydrogenation at a uniform rate and using temperatures of about 200°C. with a relatively inactive or special nickel:chromium or aluminium catalyst gives hydrogenated oils which are resistant to reversion (62,65,86). A patent to Lever Bros. (92) claims improved stability in soybean oil hydrogenated with a mixed catalyst containing one or both of copper and silver and one of chromium, vanadium, tungsten, and uranium.

f. Oxidation of revertible substances

Young and Black (136) claim to have prevented reversion in hydrogenated soybean oil by oxidizing with air at about 150°C. and then deodorizing.

4. Judgment of Flavours and Odours

Special methods are employed in judging the quality of foods such as milk products, but no report has been found which deals with methods of estimating flavour reversion in

fats or oils.

Many types of scales have been used to express the organoleptic judgment of quality. In judging oxidized flavours in milk, Trout et. al. (108) have a scale of four points (+1 to +4) and a scale of twenty-six points (from 0 to 25) in different tests. They do not consider the nature of the scale of great importance but stress the need for the judges to exert a considerable mental effort, this factor being most important in explaining the success of the better judges.

Wilson and Slosberg (134) describe a procedure for judging quality in egg powders. They use the British system of rating for scoring the flavour. This is a ten-point scale with each point described briefly so as to reduce the differences in scoring any sample both between judges on the same day and between judgments of a single judge on different tests. The scale used for egg powders is as follows:

10 -- Excellent	}	Suitable for household use
9 -- Very good		
8 -- Good		
7 -- Slight storage flavour		
6 -- Storage flavour		
5 -- Slight off flavour	}	Not acceptable for household use
4 -- Definite off flavour		
3 -- Old and unpleasant		
2 -- Very old and unpleasant		
1 -- Inedible		

Three or four judges were considered sufficient to constitute a panel. The same scale has been used by Thistle and co-workers (91,104) in judging egg powders. They found that although a panel of seven persons gave a fairly good judgment, at least fourteen persons are necessary to obtain a sound rating.

III. METHODS

A number of the methods most frequently used are described here. Other methods less frequently used and requiring only brief description, will be detailed under "Experimental".

A. REFINING

1. Alkali Refining

In all alkali refining operations a 30 per cent solution of sodium hydroxide in water was added to the oil (or shortening) in an amount about 6 to 7 per cent in excess of that required to neutralize the free fatty acids present. When refining an oil, the mixture was agitated by rapid stirring at room temperature for 45 minutes, by slow stirring at 65-70°C. for 30 minutes, and then was allowed to stand overnight at room temperature. In refining a hardened shortening the whole operation was carried out at 65-70°C. with rapid stirring for only 10 minutes followed by slow stirring for 30 minutes and allowing to stand for 10 hours at 65°C. In both cases the soaps were separated by filtration with suction. The solid soaps formed a firm mat on the filter and the oil was repassed through this. The free fatty acids were reduced to 0.02 to 0.04 per cent (as oleic acid).

2. Bisulphite Refining

This was carried out in a manner similar to alkali refining but using 5 cc. of a 10 per cent solution of sodium

sulphite in water per 100 g. of oil. Agitation was slightly less rapid in the first stage to avoid the formation of an emulsion. On settling, an aqueous layer appeared with very little solid foots; the supernatant oil layer was decanted and filtered.

3. Adsorbent Refining

a. Silica gel-alumina adsorbent

One hundred grams of silica gel (Sternson Laboratories, Brantford, Ont.) was ground to 100 mesh and added with stirring to a solution of 55 g. aluminium nitrate nonahydrate in 400 cc. of absolute ethyl alcohol in a large evaporating dish. The dish was placed on a steam bath and the mixture stirred to remove the alcohol; then dried in an oven at 100°C. and finally heated in a muffle furnace at 750°C. for three hours.

To prepare the filter, the adsorbent was spread to a depth of about one inch over a filter paper in a Buchner funnel of 2½ inch diameter. About 200 g. of oil was allowed to percolate through by gravity and about 65 per cent of it passed through the column. This oil was perfectly clear and had only a very slight colour and odour. A further 15 per cent could be recovered with suction, but this oil was slightly coloured and was not used in any of the tests.

The adsorbent was recovered by washing out the residual oil with Skellysolve B and re-heating in a muffle furnace at 750°C. for three hours. The reclaimed adsorbent was less active; the filtered oil being slightly more colored but the

difference was not marked and the product was used in some of the tests.

b. Filtrol-carbon adsorbent

A special Filtrol and an activated carbon, Darco G-60, were obtained from Mr. W.H. Lemon (Ontario Research Foundation) and mixed in the proportion of approximately 5:1 (83.4 g. of special Filtrol to 16.6 g. Darco G-60). This was added to the oil at the level of 3.6 per cent and the mixture agitated vigorously for 30 minutes at 65-70°C. The oil was then filtered with suction, the adsorbent forming a firm mat through which the oil was repassed.

This adsorbent was not recovered, a fresh portion being used for each experiment.

A number of the shortenings studied were refined with this adsorbent refining by Mr. W.H. Lemon using essentially the same procedure as that described above.

B. PREPARATION OF CATALYSTS

The catalyst used throughout this work was prepared by the dry reduction of nickel carbonate on a silica gel base as described by Hilditch (53 pp.409-10) but silica gel (ground to 100 mesh) was used in place of kieselguhr (67). Reduction was carried out at approximately 500°C. for two hours, the combustion tube being rotated frequently to ensure the complete reduction of the product. The first catalysts prepared were stored in carbon dioxide and the later ones in a small amount of hydrogenated linseed oil or Domestic Shortening.

The nickel content of these catalysts (by calculation) was 28 per cent if stored and weighed dry, and about 14 per cent if stored in the hydrogenated fat.

C. HYDROGENATION

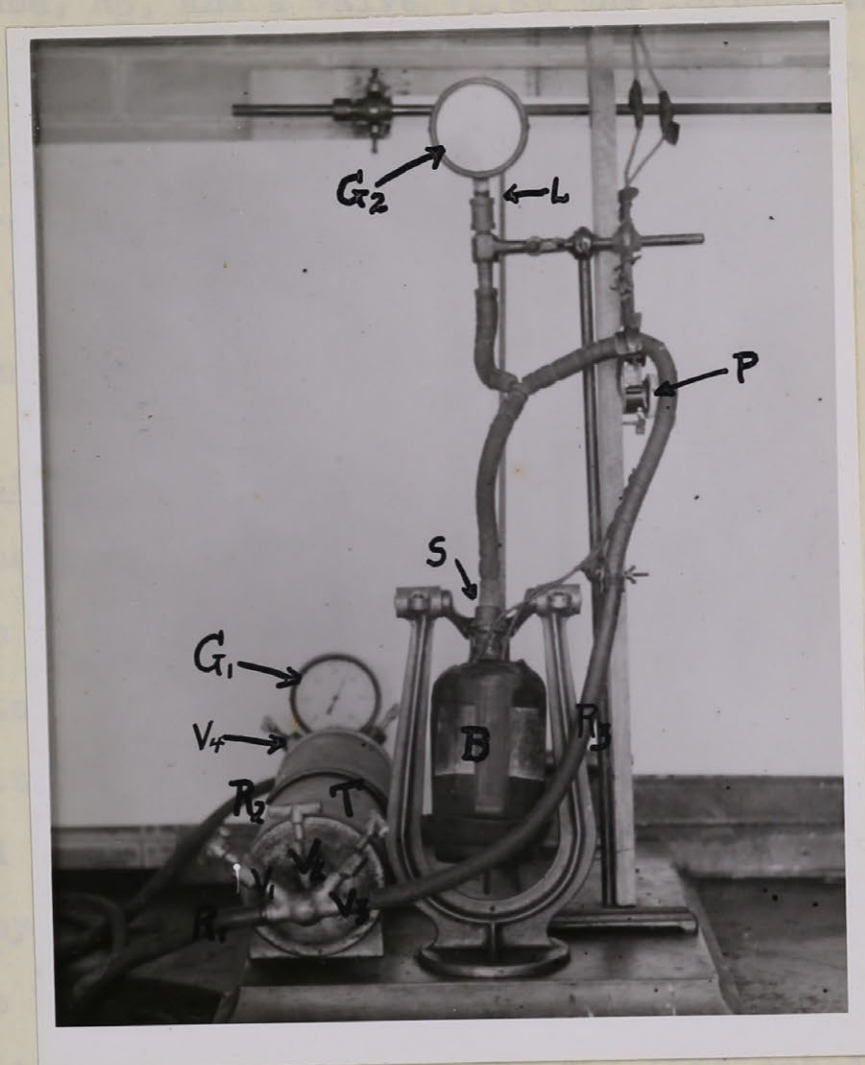
1. The Apparatus

An eccentric-driven shaker-type apparatus manufactured by the Standard Calorimeter Co., East Moline, Ill., U.S.A., was used for hydrogenation (Figure 1).

The reaction takes place in a pyrex bottle, B, of 500 cc. capacity, which is heated by a coil of nichrome wire wound around the outside of the bottle between layers of asbestos paper. The reaction temperature can be changed and adjusted by means of a light-bank rheostat in the circuit (not shown in the picture). The electric current is conducted to the reaction bottle from this rheostat by means of the wiring, W. The wiring of the bottle is connected with the remainder of the circuit at the plug, P. The switch in the circuit is on the rheostat board and is not seen in the picture. A screw, S, (behind the bottle) holds the stopper in the bottle and at the same time fastens the bottle firmly in the shaking frame. The storage tank for hydrogen, T, is of about 3.5 l. capacity (approximately 10 cm. diameter and 45 cm. long). It is connected with B, via the valves V_2 and V_3 , and the thick-walled rubber tubing R_3 . When V_2 is closed and V_1 and V_3 open, a continuous passage is formed which by-passes the tank, T, and suction may be applied on the thick-walled rubber

Figure 1

HYDROGENATION APPARATUS



- B - Hydrogenation bottle
- G₁ and G₂ - Pressure gauges
- L - Leather belt to drive shaft
- P - Electric plug
- R₁, R₂, and R₃ - Thick-walled rubber tubing
- S - Screw which holds bottle on frame
- V₁, V₂, V₃ and V₄ - Valves on tank
- W - Wiring to light-bank rheostat

tubing, R_1 , to evacuate the bottle, B. A water pump (not shown in the picture) supplied the suction. The tank, T, is filled with hydrogen from a cylinder via the thick-walled rubber tube, R_2 , and a valve, V_4 , at the farther end of T. The gauge, G_1 , shows the pressure of hydrogen in T, and the gauge, G_2 , shows the pressure in B, both reading in pounds per square inch. The leather belt, L, is shown in position to drive the eccentric wheel from the drive shaft above and behind the apparatus.

2. Operation

A charge of 100 or 200 g. of oil with the catalyst was placed in the reaction bottle and the screw tightened to fix the bottle in position. Then the bottle was evacuated, filled with hydrogen to about 30-40 pounds pressure, again evacuated to remove the air more completely, and finally filled with hydrogen to the desired pressure for the hydrogenation. The valve V_3 was closed and the agitation started. After a short period required to heat the oil (indicated on G_2 by a rise in pressure) the reaction commenced and the pressure began to fall.

Two techniques were employed with regard to the pressure of hydrogen during the reaction. The first method kept the pressure approximately constant at 15 pounds per square inch so that the reaction was taking place at an absolute pressure of approximately two atmospheres. It was possible to hold the pressure within 2 pounds per square inch by giving frequent attention to the regulation of the valves. With V_1 closed

and V_3 open a setting of V_2 could be found that would admit hydrogen at approximately the same rate as it was being consumed.

The second method of operation allowed the pressure to vary during the reaction. The valves V_2 and V_3 were opened after the initial warming period so that the pressures in B and T were the same. As hydrogen was consumed in the reaction the pressure gradually fell. The reaction was usually started at a pressure of about 35 pounds per square inch and allowed to continue until the pressure reached 10 pounds per square inch. If more hydrogen were required the tank T was quickly filled again to a pressure of about 35 pounds and the reaction continued.

The course of the hydrogenation was followed by noting the fall in pressure on the gauge G_1 which had been calibrated in terms of volumes of hydrogen. In some experiments information concerning the rate of hydrogenation was of interest. In these cases a record was made of the pressure at different times during the reaction. From the calibration of the apparatus these data could be expressed in terms of the volume of hydrogen consumed and thus the iodine number of the oil could be calculated. For most of the hydrogenations a careful study of the progress of the reaction was of no practical value, and the gauge pressure was watched only so that the reaction might be stopped when the oil had been hydrogenated to the desired iodine number.

At the end of the reaction, the shaking was stopped, the

pressure in B released by closing V_2 and opening V_1 and V_3 , and the electric current to the heating coil turned off. The screw, S, was removed and the wiring to the bottle disconnected at the plug, P, so that the bottle could be removed from the frame. The hydrogenated oil was then filtered by pouring the hot oil-catalyst mixture onto a filter paper in a Buchner funnel and sucking dry; a good pad was formed through which the sample was refiltered. Clear filtrates could thus be obtained before the oil had cooled. A sample was taken to determine the iodine number and the remainder was transferred to a round-bottom flask (500 cc.) preparatory to deodorization.

3. Adjustment of Temperatures

The apparatus permitted heating the oil at different temperatures. The rheostat consisted of a number of lamps (up to six) wired in parallel, and it was in series with the heating coil. Changes in the number and wattage of the lamps made possible the following adjustments of temperature:

<u>No. of Lamps</u>	<u>Size of Lamps (watts)</u>	<u>Temperature of Oil ($^{\circ}\text{C.}$)</u>
6	200	230
6	150	180
5	150	152
4	150	123
3	150	83
2	150	52

The temperature was determined by placing a thermometer in the hydrogenation bottle as soon as the stopper had been removed.

4. Calibration

The volume of hydrogen released when the pressure dropped a known number of gauge divisions was measured as follows:

The stopper which fits into the bottle was replaced by a short tight-fitting rubber tube which was closed by means of a clamp; and the tank was filled with hydrogen to a pressure of 40 pounds per square inch. The valve V_1 was closed and the valves V_2 and V_3 opened so that the pressure recorded on the gauge G_1 was that of the hydrogen which filled the tank and the passages through which hydrogen would normally pass right up to the bottle B. Then the portion of the tube R_3 between the gauge, G_2 , and the bottle was immersed in water in the sink with the tip under the mouth of an inverted 10-l. bottle, previously filled with water. The reading on the gauge, G_1 , was recorded and the clamp on the tip carefully opened to admit hydrogen which was allowed to escape from the tank until the bottle was exactly full when the mouth was raised to the water level. A record was then made of the pressure reading on G_1 , the temperature of the water (and hence the temperature of the gas), the barometric pressure and the exact volume of the 10-l. bottle. The procedure was repeated, i.e., another 10-l. of gas was collected with the fall in pressure, etc., recorded.

A factor for the conversion of gauge readings to volume of hydrogen at N.T.P. was calculated from the following data:

Observed barometric pressure	752.5 mm.
Temperature: 22.7°C.	
Temperature correction (brass scale) to 0°C.	<u>2.8 mm.</u>
Corrected barometric pressure	<u>749.7 mm.</u>
Volume of 10-l. bottle	10820 cc.

Trial	<u>Gauge Readings</u>			Temp. of H ₂ (°A)	Vapour Pressure of H ₂ O (mm.Hg)	Pressure of H ₂ (cor.) (mm.Hg)	Volume of H ₂ (cc.at N.T.P.)	Volume of H ₂ (cc.at N.T.P.) per gauge division
	1st.	2nd.	diff.					
1	49.0	11.8	37.2	290.5	15.0	734.7	9820	264
2	42.2	5.1	37.1	292.0	16.5	733.2	9740	262

The calculated conversion factor (exclusive of bottle) is therefore 1 gauge division = 263 cc. of hydrogen at N.T.P.

If the pressure in the bottle was kept constant during the operation of the apparatus, this conversion factor was adequate regardless of the volume of the charge or of what the actual pressure might have been. This is evident since after the charge and the bottle had been raised to the operational temperature the volume of hydrogen present in the bottle (cc. at N.T.P.) remained constant to the end of the reaction. The drop in gauge pressure then accounted for all the hydrogen absorbed.

This was not the case however if the pressure in the

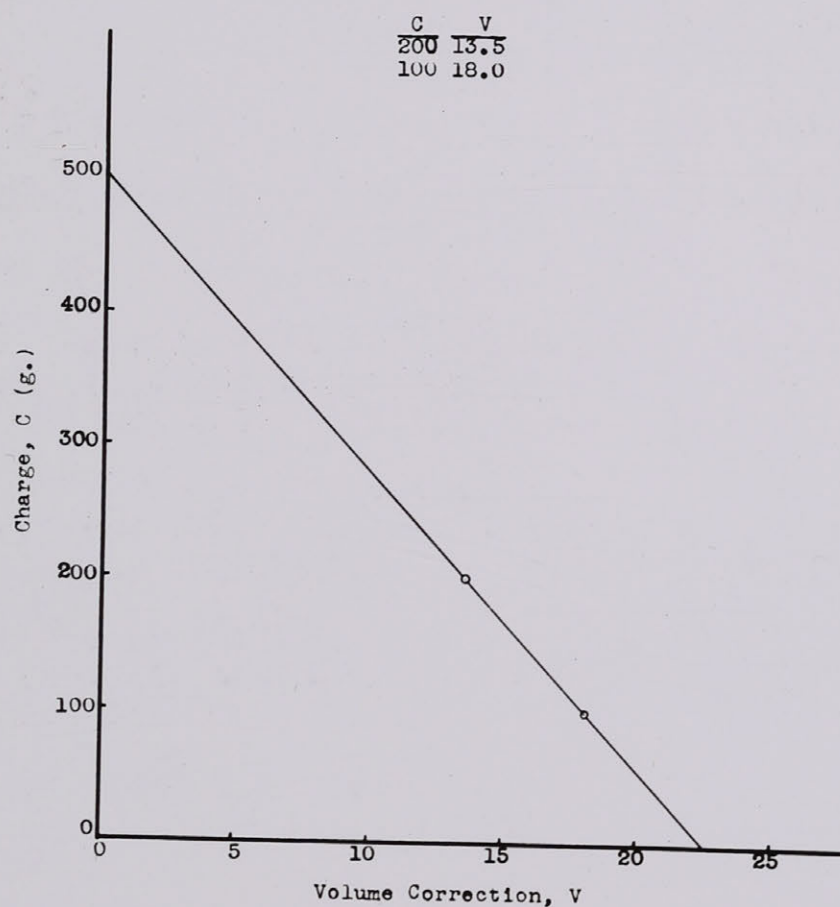
bottle fell with the pressure in the tank. In this case the volume of hydrogen in the bottle (cc. at N.T.P.) at the end of the reaction was less than at the beginning. To correct for this, the volume of the reaction bottle was determined and a relationship calculated to give the necessary correction for any size of charge. The calculations for charges of 100 g. and 200 g. are given below:

	<u>For 100 g. charge</u>	<u>For 200 g. charge</u>
Volume of bottle	550 cc.	550 cc.
Approximate volume of charge	110 cc.	220 cc.
Residual space in bottle	440 cc.	330 cc.
This is the volume at 450°A. and at pressure (lbs. per square inch) = gauge pressure (P) + 14.7(1 atmosphere).		
Volume of hydrogen at N.T.P. to fill this residual space is (P+14.7) multiplied by the factor	18.02 cc.	13.53 cc.
Correction: Approximate decrease in volume (cc. at N.T.P.) of hydrogen for 1 division on gauge =	18 cc.	13.5 cc.
Corrected factor: 1 division in terms of volume (cc. at N.T.P.) of hydrogen =	281 cc.	276.5 cc.

These correction factors were plotted and it was found that they lay on a straight line which passed through the point of zero correction for a charge of 500 grams -- a full bottle (Figure 2). Thus, as would be expected, the correction was linear. The equation of the straight line was found to be:

$$V = 22.5 - 0.045 C$$

Figure 2
 CALIBRATION CURVE
 $V = 22.5 - 0.045C$
 V = correction for volume of bottle
 C = charge in bottle (grams)



where V is the volume correction, and C is the weight of the charge in grams. The corrected factor equating 1 division on the gauge in terms of volume (cc. at N.T.P.) of hydrogen could now be easily obtained for any size of charge by adding to the factor 263 a correction determined from this equation.

From the above factors for conversion of gauge readings to volume of hydrogen absorbed, factors were then calculated for converting the gauge readings to indicate the drop in the iodine number of the oil. The iodine number of an oil is the number of grams of iodine which may be absorbed by 100 g. of the oil.

Thus, 1 unit iodine number = 1 g. of iodine absorbed by 100 g. of oil.

= 0.00781 g. of hydrogen absorbed
by 100 g. of oil.

= 87.5 cc. (at N.T.P.) hydrogen
absorbed by 100g. of oil.

That is, 87.5 cc. (at N.T.P.)
of hydrogen absorbed per 100
g. of oil = 1 unit drop in iodine number.

or, 1 cc. (at N.T.P.) of
hydrogen absorbed per 100 g.
of oil = 0.01142 drop in iodine number.

If the apparatus were operated at constant pressure (1 gauge division = 263 cc. of hydrogen at N.T.P., then a pressure drop of 1 gauge division per 100 gram of oil would indicate an absorption of 263 cc. (at N.T.P.) of hydrogen per 100 grams and a drop in iodine number of $263 \times 0.01142 = 3.02$ units. If the apparatus were operated with the pressure

decreasing, the hydrogen volume equivalent to a gauge division (Figure 2) multiplied by 0.01142 gives the drop in iodine number for a pressure drop of 1 gauge division per 100 g. of oil.

To simplify the calculations a graph was prepared (Figure 3) showing the hydrogen volumes (V) which are equivalent to 1 gauge division plotted against the drop in iodine number (D) for a pressure drop of 1 gauge division per 100 g. of oil.

5. Rate of Reaction

From the hydrogenation runs in which a record was kept of the volume of hydrogen absorbed at various time intervals it was possible to make some observations regarding the reaction rate.

A reaction is of zero order if the rate is unaffected by the concentration. This may be expressed by

$$\frac{dc}{dt} = K_0$$

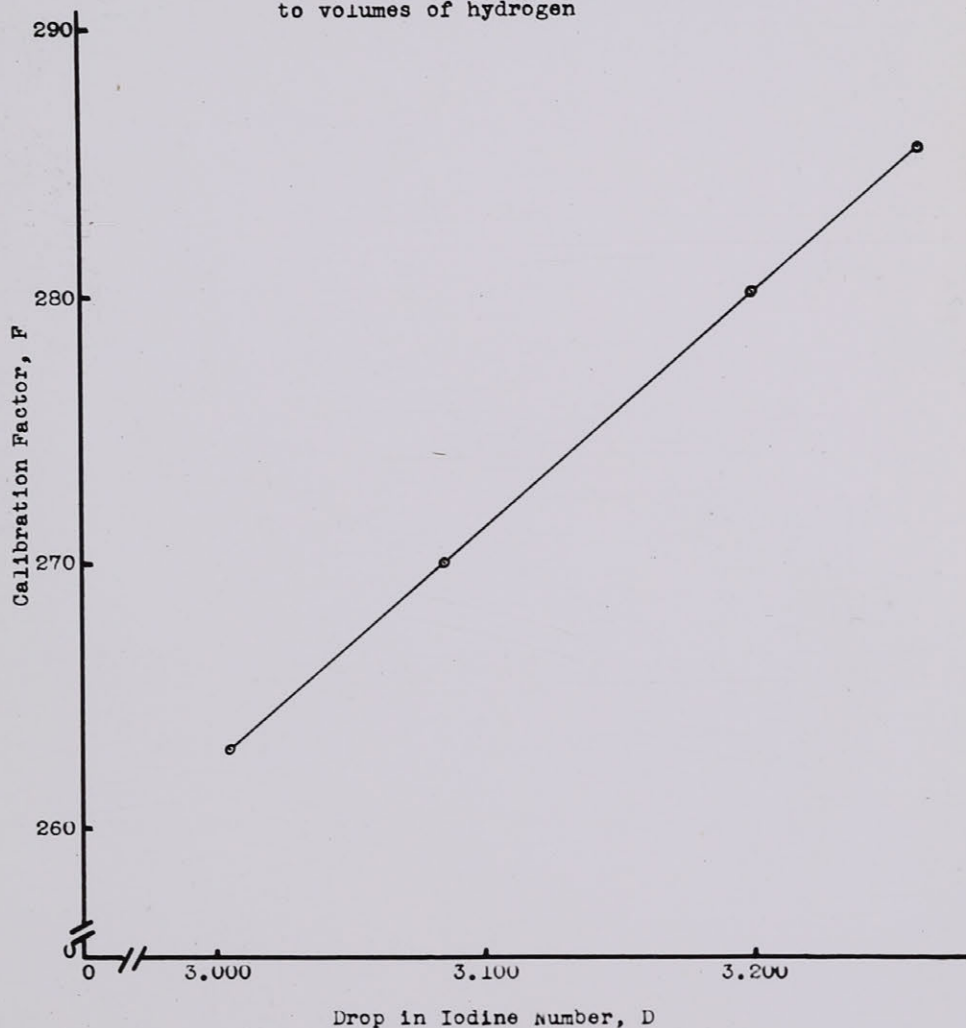
where c represents the concentration of the reacting substance, t represents the time and K_0 is the zero order reaction constant. If this describes the conditions then concentration plotted against time gives a straight line.

A reaction is of first order if it is found that the rate is directly proportional to the concentration of the reacting substance. This may be described as

$$\frac{dc}{dt} = k_1$$

Figure 3
CALIBRATION CURVE
 $D = 0.01142F$

D = drop in iodine number for pressure drop
of 1 gauge division per 100 g. of oil
F = factor calibrating gauge divisions
to volumes of hydrogen



which on integration becomes:

$$- \log c = K_1 t + \text{constant}$$

Again c is the concentration of the reacting material, t is the time and K_1 is the first order reaction constant which includes the factor 2.303 converting Napierian logarithms to common logarithms. If these conditions obtain the log. of the concentration plotted against time gives a straight line.

In this work the unsaturated fatty acids were the reacting substances and their concentration at intervals during the reaction was calculated as indicated above from the iodine number and hydrogen absorbed. This value was plotted against time, and the log. of the concentration was also plotted against time.

D. DEODORIZATION

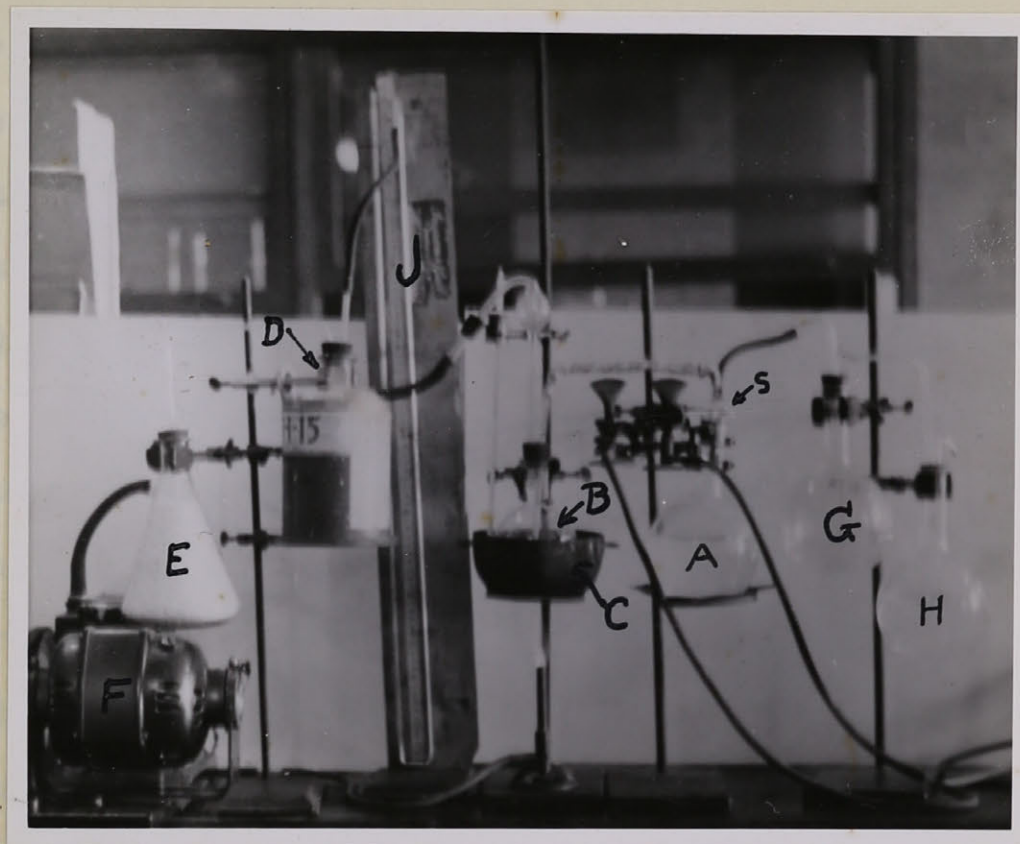
Some of the first deodorization treatments were carried out by bubbling carbon dioxide or nitrogen through the fat at 200°C. for three hours while the pressure was kept at five mm. or less with a Hyvac pump.

Steam deodorization was carried out in the apparatus depicted in Figure 4.

The stopcock, S, is closed and water vapour is passed from this flask A through the heated and asbestos-covered pyrex tube to escape through a jet into the shortening in the flask B. A sufficient volume of steam is evolved and passed through the oil by having the water in flask A at a moderate temperature since the vapour pressure of water at 20°C. is

Figure 4

DEODORIZATION APPARATUS



- A - Source of water vapour.
- B - Flask containing fat, with a jet for steam.
- C - Oil bath.
- D - Ice-water trap.
- E - Calcium chloride trap.
- F - Hyvac pump.
- G and H - Flasks serving as a valve to regulate the release of the vacuum.
- J - Manometer.
- S - Stop cock.

17.5 mm. Hg (50 p.1061). The temperature of flask, B, is maintained at 200°C. by the oil bath, C, The escaping vapours pass through a trap and are condensed in the flask, D, surrounded by an ice-water bath and the remaining traces of water vapour are held by calcium chloride in flask, E. A mercury manometer, J, is connected to flask, D, and by subtracting from the barometric pressure the difference in the mercury levels in the two arms, the actual pressure in the flask, D (or C) is obtained. Since the vapour pressure of the water in the ice trap is 4.6 mm. (50 p.1060), this is the lowest pressure theoretically possible with this apparatus. The apparatus seemed satisfactory since with the Hyvac pump, F, the pressure was constantly close to 5 mm.

The flasks, G and H, facilitate the release of the vacuum without permitting the deodorized shortening to come in contact with air. The flask, G, is fitted with a rubber stopper having three tubes passing through it and is nearly filled with water. With S closed, nitrogen is blown gently into the flask forcing all the water into flask, H, and finally to wash the small amount of air out of the flask. The gases bubble through the water in H and escape. When the deodorization is complete the flames are turned off, the oil bath is removed, the pump is stopped, and while the nitrogen gas is passing into G, the stopcock, S, is opened. This permits nitrogen gas to pass through the apparatus blowing out the water vapour, releasing the vacuum and partially cooling the oil. With some adjustment of the stopcock, S and only very coarse

regulation of the flow of nitrogen into flask G, the "valve" formed by the flasks, G and H, makes it easily possible to control the release of the vacuum.

The product in flask C was frequently coloured after deodorization but this could easily be removed by adding about 5 per cent of a filter aid and filtering through a "Buchner funnel. Silica gel adsorbent was generally used but Super-cel Standard was also employed.

An improved design of apparatus has been described by Bailey (8) which would be advantageous for a study of the compounds removed in deodorization.

E. ANALYTICAL PROCEDURES

1. Acid Value

The A.O.A.C. method (81 p.417) was followed with the exception that samples of 5 g. were frequently used with 15 cc. of ethyl alcohol when the amount of material would not permit taking the regular 20 g. samples. Titration with N/100 sodium hydroxide was preferred to N/10 alkali when the free fatty acid content was low.

2. Iodine Number

The method of Rosenmund and Kuhnhehn (101) was used with a number of modifications. It is here described in detail.

a. Reagents

(1) Pyridine sulphate dibromide (Brominating reagent). Eight grams of pyridine and 10 g. of sulphuric acid were dissolved in

20 cc. of glacial acetic acid. To this was added a solution containing 8 g. of bromine in 20 cc. of glacial acetic acid. The mixture was diluted to one l. with glacial acetic acid.

(2) Starch solution. A paste of 5 g. of soluble starch with about 10 cc. of water was prepared and poured into 500 cc. of boiling water to make a 1 per cent solution. Then 75 g. of potassium chloride was dissolved in this solution to protect it from bacteria. The final solution was stored under a layer of toluene in a stoppered bottle.

(3) Thiosulphate solution. Crystalline sodium thiosulphate was dissolved in recently boiled water (24.82 g. to one l. of water). The solution was made just alkaline to phenolphthalein with sodium hydroxide, and stored in a carefully-cleaned brown bottle fitted with a siphon delivery and a soda-lime tube to absorb carbon dioxide. This solution, approximately one-tenth normal, was frequently standardized with potassium dichromate (42 p.354-5).

(4) Potassium iodide solution. A 10 per cent solution of potassium iodide was freshly prepared for each set of determinations as the solutions darkened on standing.

b. Method

About 0.1 g. of the sample was weighed accurately in a small glass bottle made by sealing a glass tube and flattening it at the sealed end so as to give a bottle of about $1/4$ in. diameter and $3/8$ in. high. The bottle plus sample was placed in the iodine flask, 10 cc. of carbon tetrachloride

added and the sample dissolved by warming gently.

Then 25 cc. of the brominating reagent was added, the stopper inserted immediately, the flask swirled and about 0.5 cc. of the potassium iodide solution added around the lip of the flask. The flask was placed in the dark for exactly 10 min. then 10 cc. of the potassium iodide solution was allowed to run around the lip of the flask while releasing the stopper to allow the solution to enter the flask. The stopper was then replaced and the flask swirled. Finally 100 cc. of distilled water was slowly added to the flask while the stopper was slightly released, and then, with the stopper returned, the flask was swirled vigorously.

The free iodine in the flask (liberated by the bromine in excess of that which reacted with the fat) was then titrated with the thiosulphate solution to a light straw colour; about one-half cc. of starch solution was added and the titration continued to the point where the last drop of thiosulphate discharged the blue colour. The stopper was then inserted and the flask shaken to mix thoroughly the aqueous and the carbon-tetrachloride layers. If a bluish colour reappeared more thiosulphate was added to decolorize the solution. A bluish colour which often appeared on standing was disregarded.

All determinations were made in duplicate and blank determinations were run in duplicate with each series to give a measure of the amount of bromine in the 25 cc. aliquot added in each test.

3. Peroxide Content

The ferric-thiocyanate method as described by Lips, et. al. (72), was employed with some minor changes in detail. In the preparation of the reagent the careful adjustment of volume seemed unnecessary so a graduated cylinder was used. The reagent was prepared in an Erlenmeyer flask which permitted easier mixing and handling than in a volumetric flask, and it was decanted from the undissolved ferrous salt instead of filtering through an acetone-washed filter paper. The fat was weighed into a 50-cc. Erlenmeyer flask instead of a beaker so that on dissolving in acetone, there would be less loss of acetone on warming. The peroxide content was expressed in milliequivalents (M.E.) of peroxide per kilogram of fat.

F. CONJUGATED HYDROGENATION

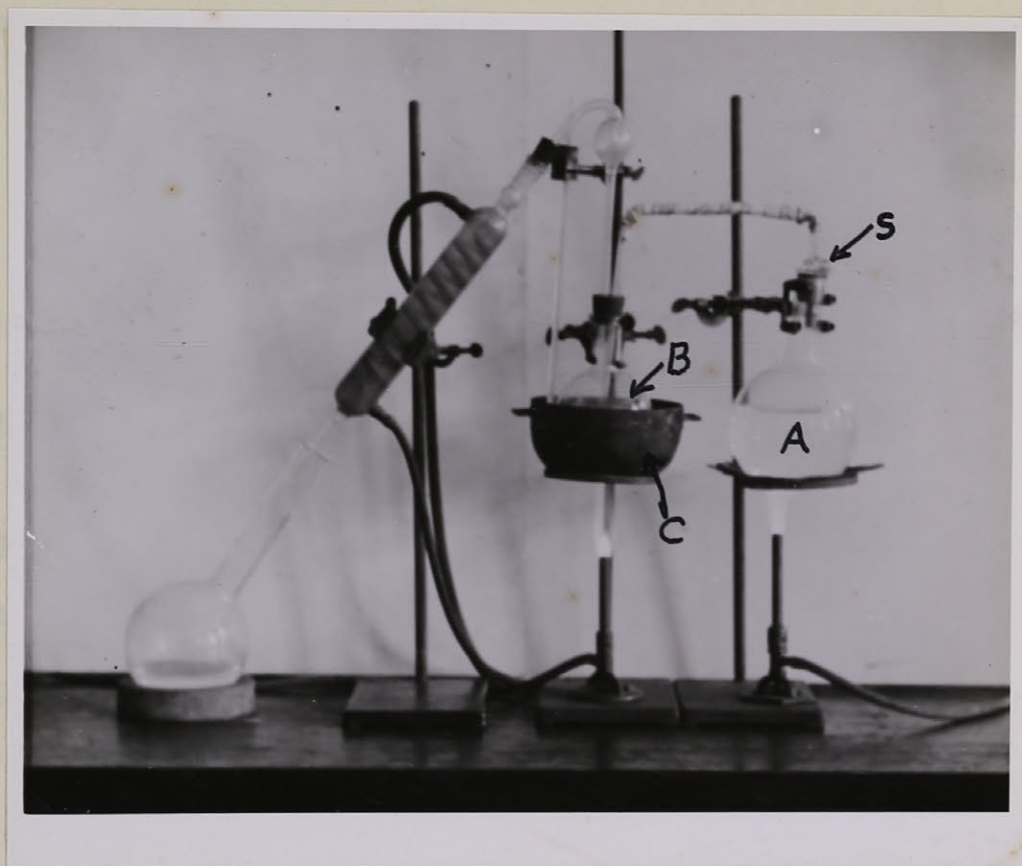
The conjugated hydrogenation experiments were carried out, at approximately atmospheric pressure in the apparatus shown in Figure 5.

In operation the stopcock, S, is closed and the stopper in flask, A, is wired down. Alcohol vapour from A passes via a jet into the oil containing the nickel catalyst in flask B, which is maintained at 180°C. by an oil bath, C. D is a water-cooled spiral condenser which recovers the alcohol. With the spiral-type condenser placed in this manner some of the liquid condensate collects in each turn of the spiral and permits a small pressure to be built up in the flask B.

To follow the course of hydrogenation the stopper in

Figure 5

CONJUGATED HYDROGENATION APPARATUS



A - Ethanol.

B - Flask containing fat with a jet for the ethanol vapour.

C - Oil bath.

D - Condenser.

S - Stop cock.

flask B, was loosened at intervals, a long glass tube inserted into the oil and a sample of about 4 to 5 g. withdrawn. The stopper was immediately replaced and the reaction continued. The sample was quickly filtered through filter paper in a Gooch crucible and if not free from catalyst, it was filtered again. This could be done quickly without the sample solidifying if the filter was warmed (75°C.) before use. The iodine number of each sample was determined to indicate the degree of hydrogenation.

G. JUDGMENT OF QUALITY OF SHORTENING

1. Quantitative Estimate by Panels

In a number of cases a panel of ten to fifteen judges was organized to quantitatively measure the quality of a particular series of samples. In some cases the flavour and in others the odour of the samples was judged. In either case, two methods were employed to assign a numerical score to each sample. In the first method a ten-point scale resembling that of Wilson and Slosberg (134) was used with the points on the scale described briefly in the following manner:

10 Excellent	}	Considered suitable for household use.
9 Very good		
8 Good		
7 Slight off flavour (odour)		
6 Off flavour (odour)		
5 Slight oily or reverted flavour (odour)	}	Considered not acceptable for household use.
4 Definite oily or reverted flavour (odour)		
3 Unpleasant flavour (odour)		
2 Very unpleasant flavour (odour)		
1 Repulsive flavour (odour)		

Each sample in a series was scored by each of the judges. The scores for each sample were then averaged. The best score possible was thus 10 and the poorest was 1.

In the second method the judges were asked simply to indicate for each sample in flavour judgment whether or not they considered it of satisfactory flavour for household use; and in the case of odour judgments, whether or not they considered it to have a reverted (or worse) odour. Then to give a rating of the "excellence" of each sample the number of judgments declaring it satisfactory (or not reverted in odour) were added and this total divided by the number of judgments, giving scores in fractional quantities. Thus with 12 judges in a panel, a sample judged satisfactory by all judges would have a score of $12/12 = 1$, and a sample judged satisfactory by 6 judges would have a score of $6/12 = 0.5$. To have these scores more nearly like those obtained by the first method each was multiplied by 10, thus the two samples mentioned would receive final scores of 10 and 5 respectively. In a number of experiments it was desired to follow the progress of reversion by noting the development of the reverted odour. In these cases it was more convenient to record for each sample the percentage of the judgments which considered it reverted. It should be pointed out that both forms of this second method graded the samples on a scale of eleven points because a very poor sample could receive a score of zero if all judges considered it unsatisfactory.

2. Flavour-Judgment by Panels

In the flavour-judgment tests which were panel-judged the samples of shortening were used by the third-year Household Science cooking-class in baking (muffins, biscuits and pastry in different tests) and the class served as the panel to judge the products. The whole class was divided into two sections, A and B, of twelve girls each, having different periods for their cooking class. Each girl prepared baked products from two samples of shortening. A complete duplicate of the baking and judging was obtained by having Section A use the 24 samples of a series and each of the 12 girls judge all of the 24 products, then at the next period, Section B used the same 24 samples and each of these twelve girls judged all of the 24 products. Also members of the staff of the Department of Household Science frequently served as judges in these panels.

In these tests all samples were placed in 250-cc. beakers with watch-glass covers and given numbers by drawing numbered cards from a box. The baked products were arranged and judged in numerical order. The numbers of a series of samples were the same for both sections. The samples were not discussed during judging, nor were they discussed with Section A at the conclusion of the judging because Section B was later to judge the same samples. To minimize differences due to baking, both sections used the same recipe, technique and baking time and temperature. Also the method of scoring judgments was the same in each section; whichever method was used, both sections used it. These quantitative measures of

quality made possible the analysis of the data by statistical methods.

3. Odour-Judgment by Panels

In these tests also the samples were randomized and none were known to the judges. These judgments were entirely for reversion-odour in samples of shortening and were never tests of baked products. Each sample consisted of about 2 to 3 g. of shortening in a Syracuse dish (approximately 2 in. diameter and 3/8 in. deep). The dishes of each series were given numbers (starting from 1) as with the other samples, and were judged in this order.

The judging panel for these tests was composed of post-graduate students in Agricultural Chemistry. All the students available were presented with samples of fresh and reverted linseed oil shortenings and twelve were chosen to form the panels because they showed themselves able to distinguish between the samples and expressed confidence in their ability to recognize the reverted odour. In addition, a test given to these judges to ascertain the reliability of their judgments indicated that all judges should be retained in the panel.

4. Qualitative Judgments

For every sample of shortening prepared in the course of this investigation, the success or failure of the process involved, lay in the answer to the question, "Does it give a reverted flavour when used in baking?". During the course of the work it was thought that it might be sufficient to

determine whether or not a sample would give a reverted odour on heating in an oven at 100°C. However this was felt to be not the real criterion of quality. Such a test would lack finality, although it might give an indication of what was probably unsuccessful.

Thus for all samples it was desired to have a baking test as a measure of the quality. In many cases samples of shortening were prepared which could not conveniently be baked and judged by the panel. The class of students could do only a limited amount of this work, and could do that only at certain times. For the samples not baked and judged by this cooking class, various individuals in the Department of Household Science gave parts of their spare time. In this manner baking was done by two girls of the third-year class, four of the fourth-year class, and one graduate in Household Science. In all these tests, pastry was prepared and the samples were judged qualitatively by the author, by the girls who cooperated in doing the baking and by a few graduate students in the Department of Agricultural Chemistry.

H. ADDITION OF ANTIOXIDANTS

The antioxidant was dissolved in a small amount of diethyl ether and this solution added to the melted shortening in a beaker at a temperature of about 65°C. The mixture was stirred thoroughly during, and for a few minutes following, this addition. The volume of ether solution was commonly 10 cc. while the amount of the fat was from 100 to 200 g. When the

fat had become appreciably cooled it was placed in an oven at 65°C. and was stirred frequently as long as bubbles of ether vapour escaped (about 45 min.). Then the remaining ether was removed in a vacuum desiccator.

IV. EXPERIMENTAL

A. MODIFICATIONS OF ESTABLISHED PRACTICE

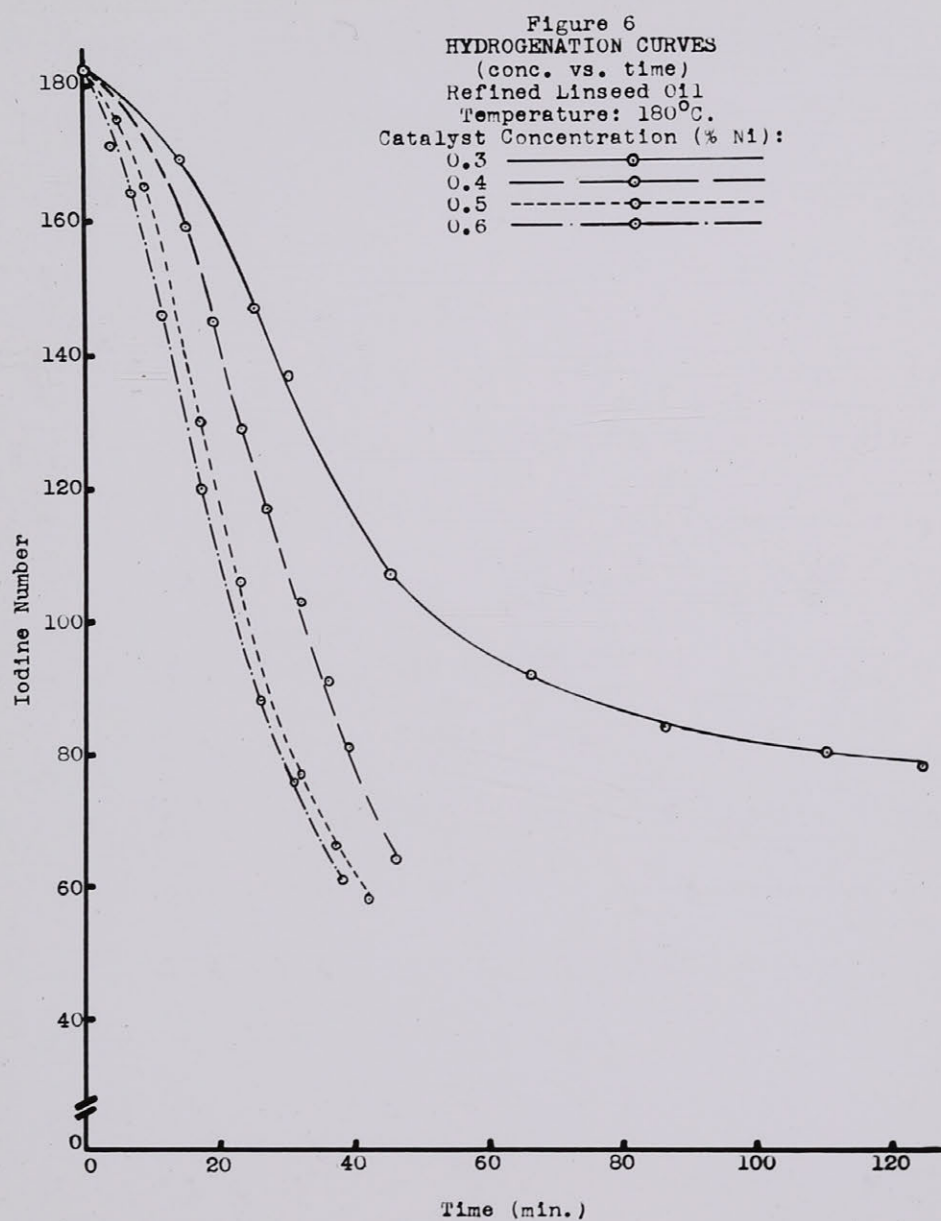
In this section will be described a number of experiments which were designed to determine whether or not it might be possible to produce a non-reverting linseed oil shortening if some modification of the usual processing methods were employed.

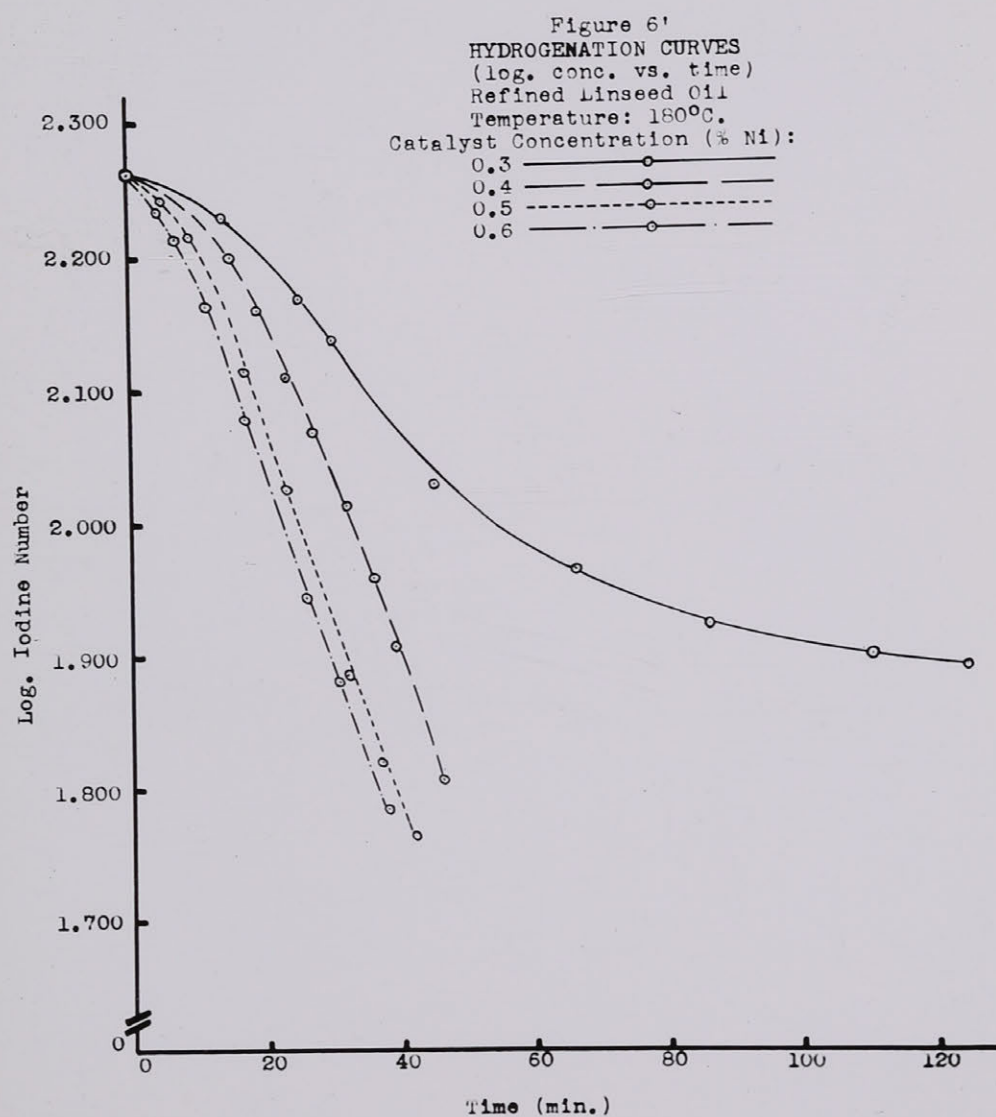
1. Effect of Catalyst Concentration

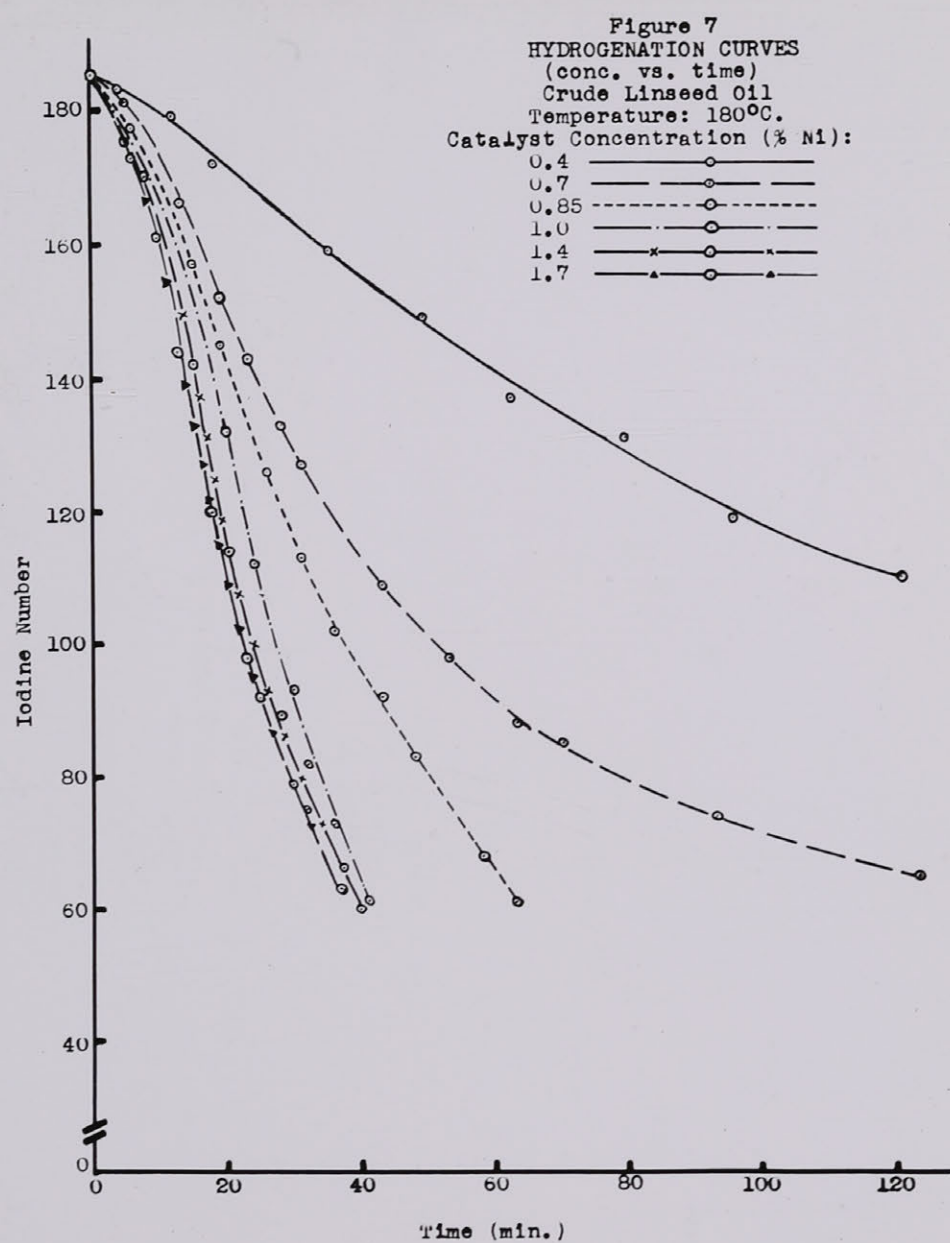
In addition to the effect of catalyst concentration on reversion, it was very early in the work found desirable to know its effect on the rate of the reaction. This information would tell what amount of catalyst was required to carry out the reaction, and to what extent the time required might be reduced by increasing the amount.

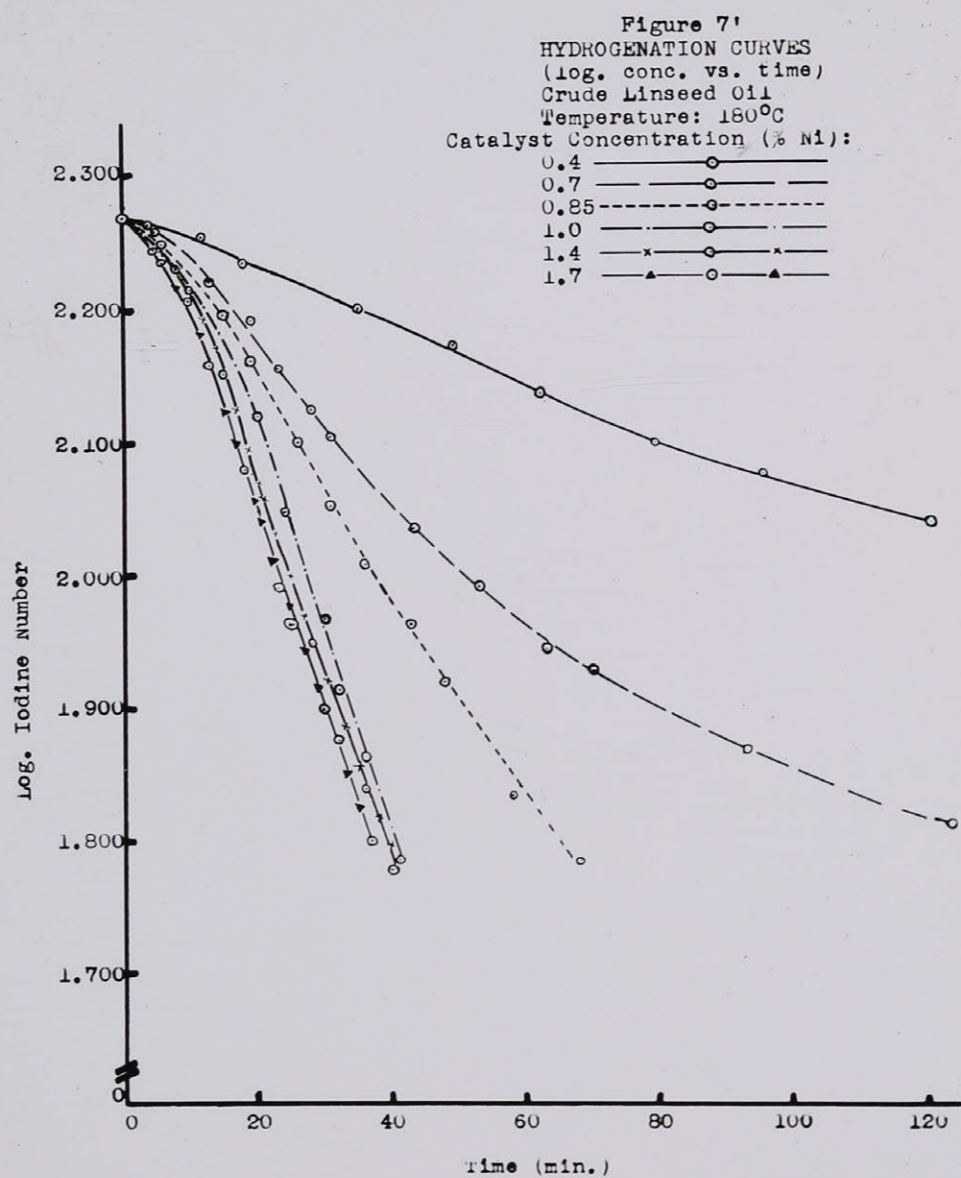
Four samples of alkali-refined hot-pressed linseed oil (each 100 g.) were hydrogenated at 180°C . with catalyst concentrations of 0.3, 0.4, 0.5 and 0.6 per cent nickel. Six samples of crude hot-pressed linseed oil (each of 100 g.) were hydrogenated at 180°C . with catalyst concentrations of 0.4, 0.7, 0.85, 1.0, 1.4 and 1.7 per cent nickel. These hydrogenations were stopped to give products having an iodine number of about 65.

The hydrogenation curves (Figures 6 and 7) show in detail the progress of the reaction in each of these experiments. The figures 6' and 7' have been prepared for the information they give concerning the reaction rate. The catalyst





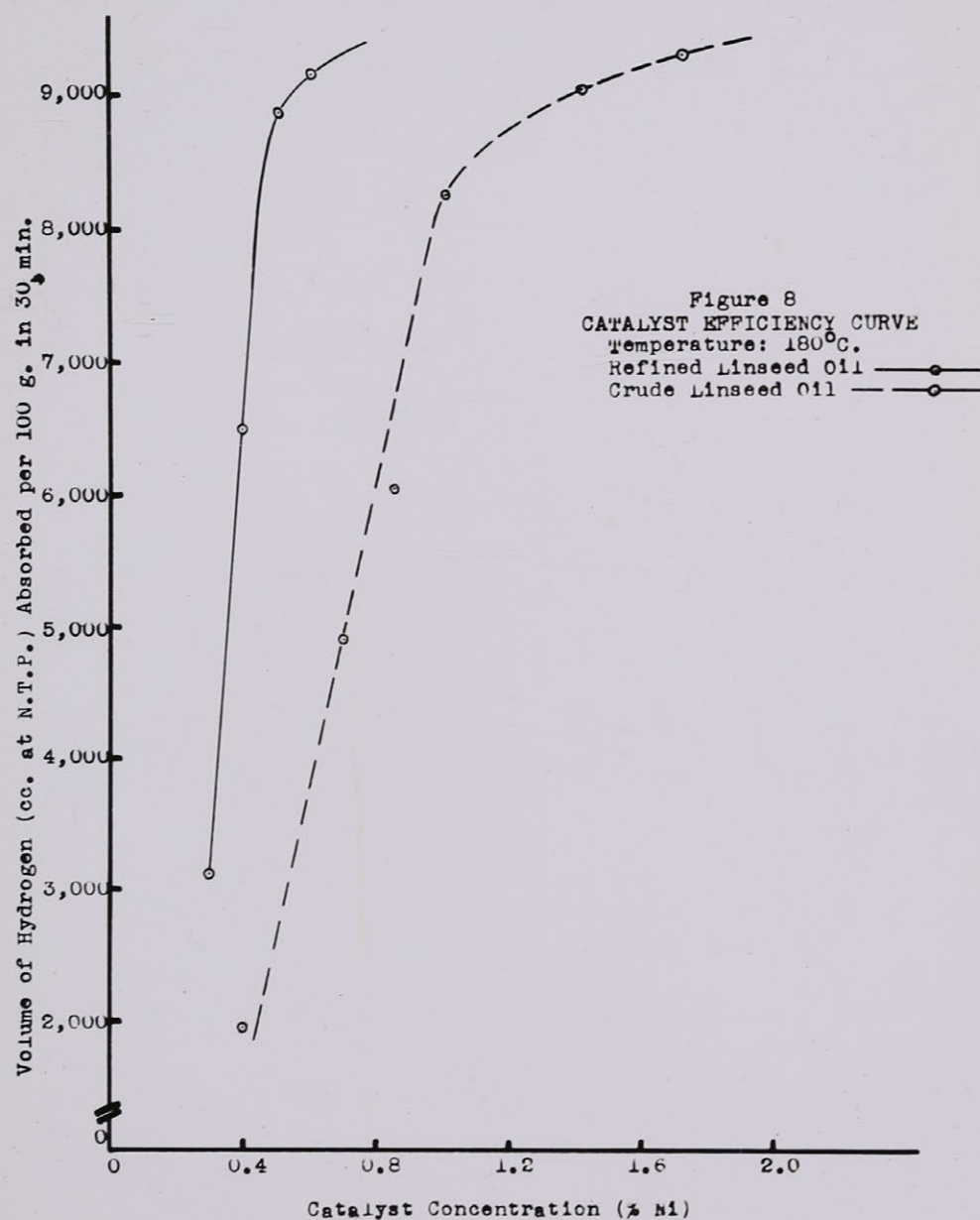




efficiency curve (Figure 8) summarizes the findings regarding the effect of increasing catalyst concentrations on increasing the rate of the reaction.

To determine the effect of varying the catalyst concentration on reversion flavour in the shortening these samples were deodorized and then used to make pastry. Qualitative judgments of the flavour indicated that the crude linseed oil gave a somewhat better shortening with increased amounts of catalyst but there seemed no difference among the shortenings prepared from the refined oil. In general the shortenings from the refined linseed oil and the better ones from the crude oil were of similar quality. However, the reverted flavour could be detected in all samples; none were free of it. Nevertheless some of the samples were considered not unpleasant and two of them were considered by some of the judges to be better than the Domestic Shortening control. The indications were not always definite since in some cases duplicate samples prepared from the same shortening differed appreciably. It was thought that differences in the amount of cooking might account for some of these differences since well-browned pastries were observed to have a better flavour than corresponding ones if not browned. An absolute control of all factors involved in the baking seemed not to be possible since these samples had been baked for the same length of time and at the same oven temperature.

On the basis of these experiments with different concentrations of catalyst, future hydrogenations of refined oils



were carried out with 0.5 to 0.6 per cent nickel catalyst and hydrogenations of crude oils were carried out with 1.0 to 1.2 per cent of nickel. These amounts were employed since they reduced the time required for the hydrogenation without wastefully using the catalyst, and also since with crude oils this amount seemed to give a better shortening.

2. Hydrogenation at Different Temperatures

It was desired to study the effect of different hydrogenation-temperatures on the quality of the shortening produced, and also to study the effect of increased temperature on the rate of hydrogenation. Five samples of an alkali-refined hot-pressed linseed oil (each of 100 g.) were hydrogenated with 0.6 per cent nickel catalyst at the following temperatures: 52, 83, 123, 152 and 180°C. The course of each hydrogenation was followed in detail and the reaction was allowed to continue to give a product with an iodine number of about 65. The details of these reactions are shown in the accompanying graphs (Figures 9 and 10). Figure 10' gives additional information concerning the reaction rate. The deodorized shortenings were of satisfactory odour and with the exception of that hydrogenated at 52°C. which was a pale yellowish-green, all were satisfactorily free of colour. There appeared no marked differences in flavour of pastry baked from them beyond those differences which existed in duplicates. All the samples had a reverted flavour, yet one of the products (from the shortening prepared at 123°C.) was preferred to the control Domestic

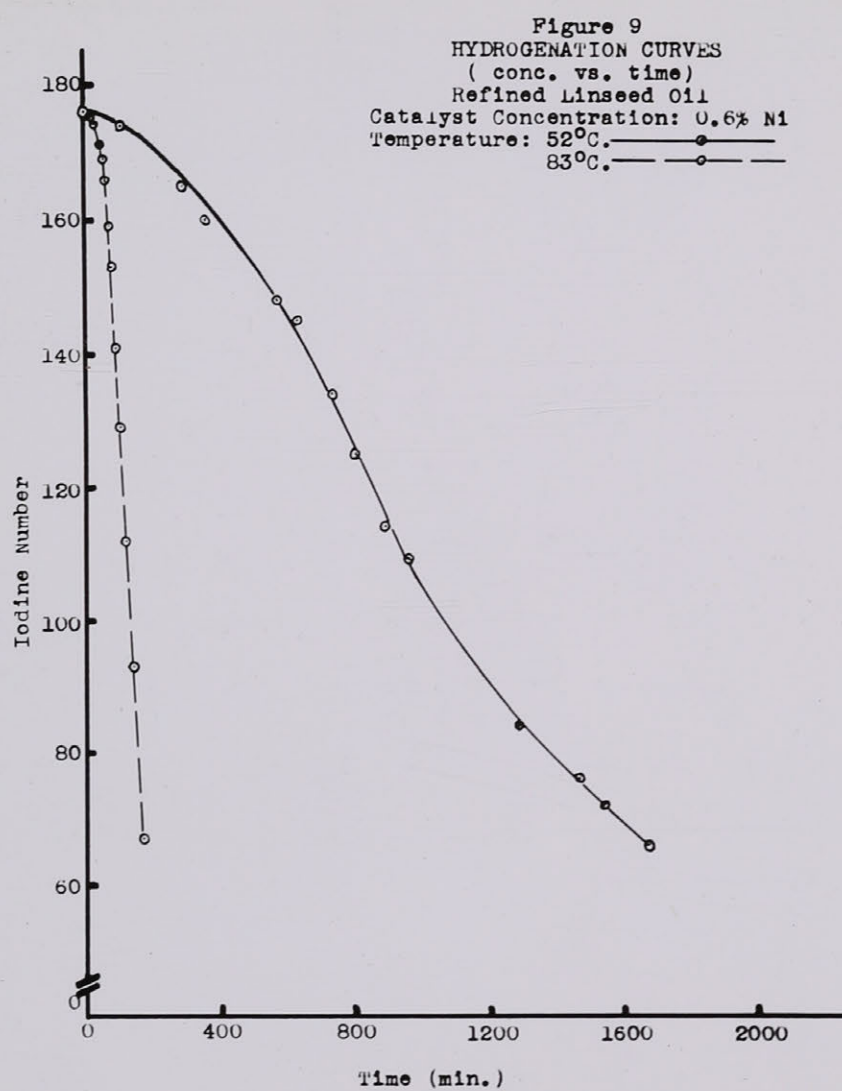


Figure 10
HYDROGENATION CURVES
(conc. vs. time)
Refined Linseed Oil
Catalyst Concentration: 0.6% Ni
Temperature: 52°C. —○—
83°C. —○—
123°C. - - -○- - -
152°C. —○—
180°C. —x—○—x—

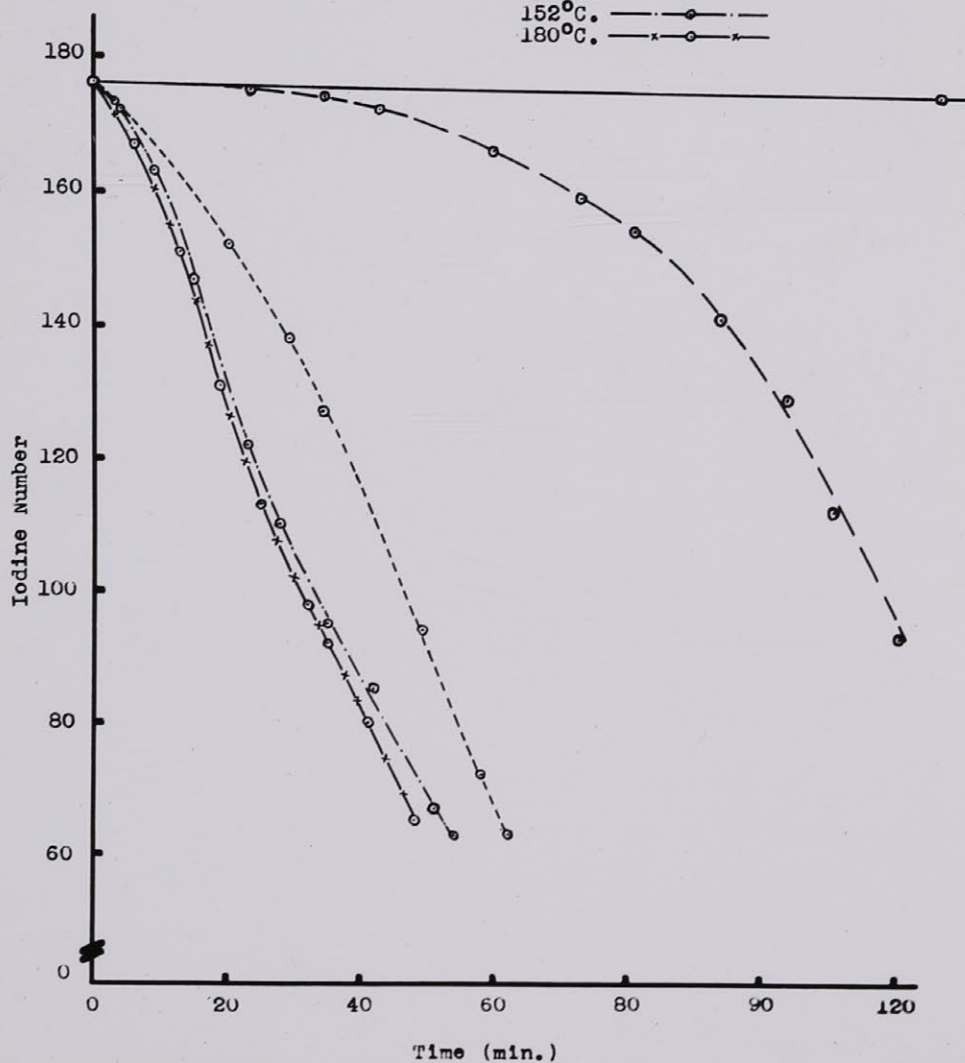
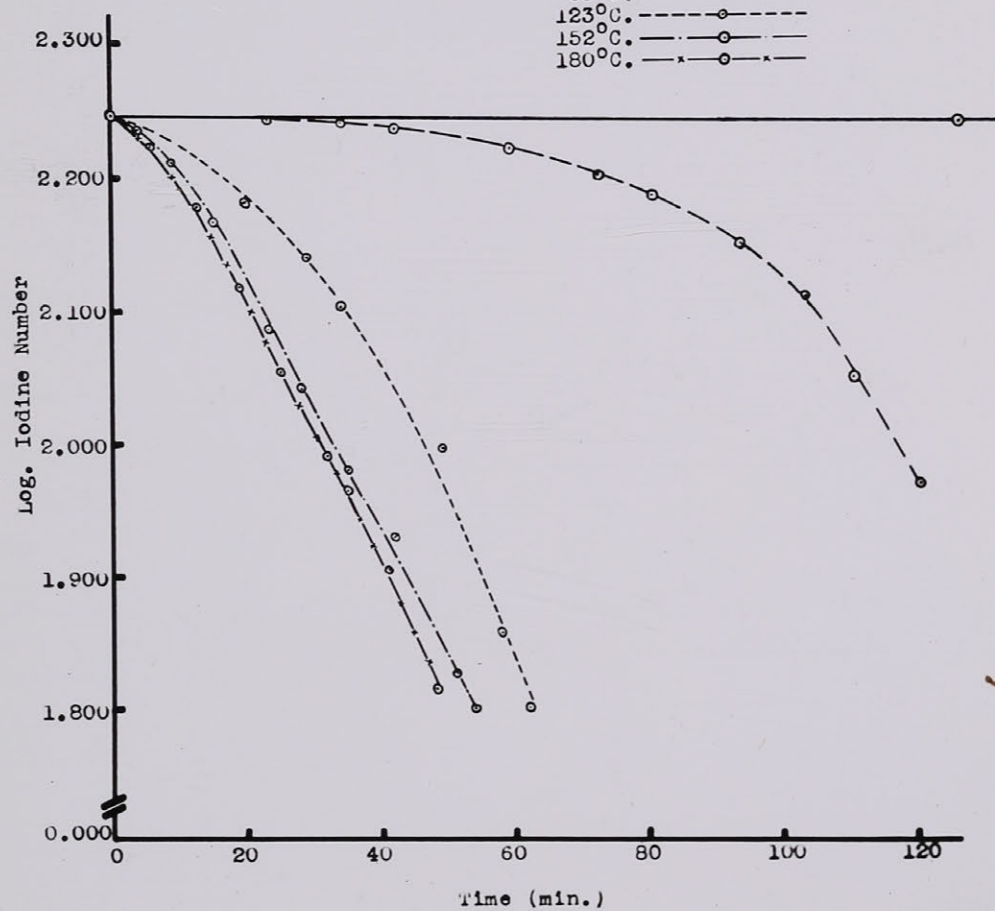


Figure 10'
HYDROGENATION CURVES
(log. conc. vs. time)
Refined Linseed Oil
Catalyst Concentration: 0.6% Ni
Temperature: 52°C. —○—
83°C. —○—
123°C. —○—
152°C. —○—
180°C. —x—



Shortening by two of the five judges, and two (from the shortenings prepared at 152 and 180°C.) were considered equally as good as the control by three judges. A definite conclusion that the higher temperatures gave better products could not be drawn since the duplicates of these "better" samples were judged no better than those samples baked from the shortenings hydrogenated at the lower temperatures.

The effect of temperature on the rate of the reaction is summarized in Figure 11 where the volume of hydrogen (cc. at N.T.P.) absorbed by 100g. of oil in 30 minutes is plotted against temperature of hydrogenation. It is shown that the reaction rate is markedly increased by increases of temperature from about 80 or 90°C. up to about 150°C. Below and above this range the effect is relatively slight.

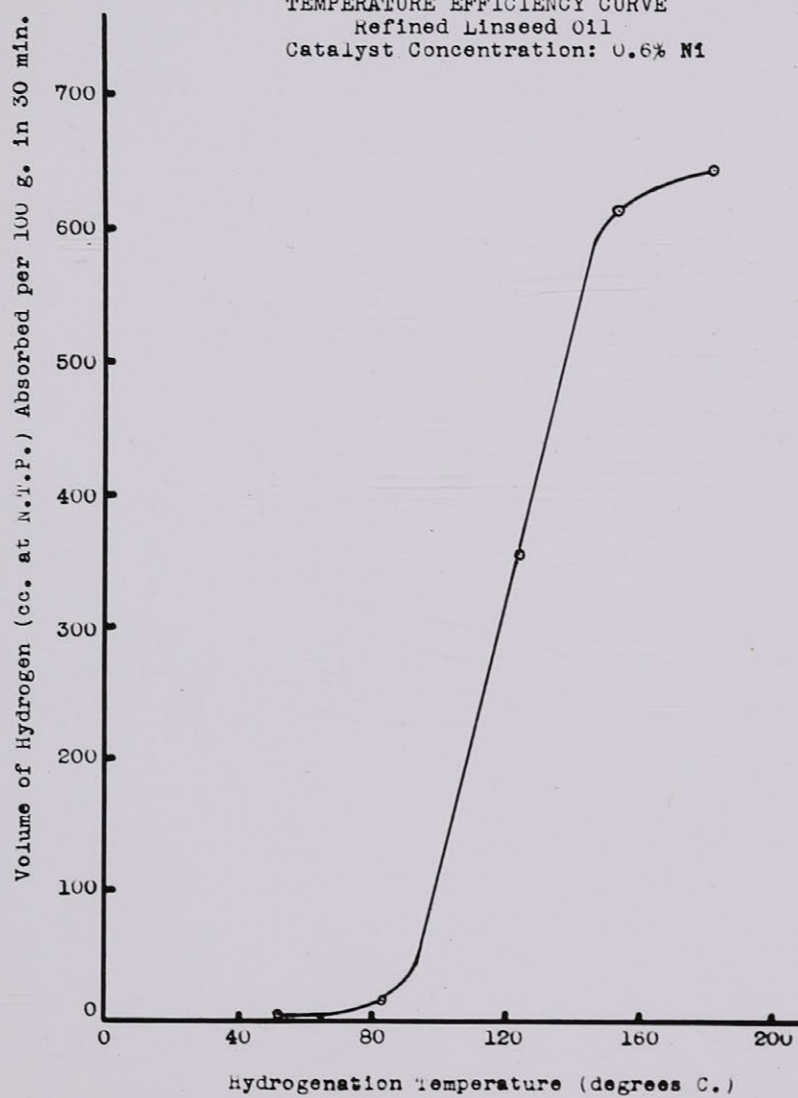
In future work, a temperature of 180°C. was used in all hydrogenations. This temperature was employed since it gave a shortening of at least as good quality as that produced at lower temperatures and since it brought, as far as seemed practical, a reduction in the time required for hydrogenation.

3. A Study of Refining Procedures

In these experiments a number of different refining techniques were studied on both a hot-pressed and a cold-pressed linseed oil. It was desired to learn whether the use of a hot-pressed oil presented any special difficulties.

Five samples of each oil were hydrogenated after the following treatments:

Figure 11
TEMPERATURE EFFICIENCY CURVE
Refined Linseed Oil
Catalyst Concentration: 0.6% Ni



- a. No treatment. The unrefined oil was hydrogenated.
- b. Alkali refining.
- c. Alkali refining, then bisulphite refining.
- d. Alkali refining, then adsorbent refining(silica gel-alumina).
- e. Alkali refining, then adsorbent refining (Filtrol-carbon).

The amount of oil hydrogenated varied between 150 and 200 g. in these experiments but the concentration of catalyst was kept at 1.0 per cent nickel for the unrefined samples and 0.5 per cent for the refined ones. All these hydrogenations were stopped where the iodine number of the sample had been reduced to about 70. All the deodorized products were of satisfactory colour and odour.

The pastries prepared from these shortenings indicate that those from the hot-pressed oil were as good as the corresponding ones from the cold-pressed oil. The shortenings from the bisulphite-refined oils gave the poorest pastry, but aside from these, it was considered that increased refining did produce some improvement in quality. Thus the samples from alkali-and-adsorbent-refined oils were considered better than those from the alkali-refined oils and these in turn better than the samples prepared from the unrefined oils. Between the two adsorbent refining techniques a slight preference was expressed for the samples refined with the silica gel-alumina.

In these judgments, as in those before, the pastry from

the Domestic Shortening control was not always considered the best. The majority of the judges actually expressed a preference for one sample of pastry prepared from the alkali-and-silica gel-alumina-refined hot-pressed linseed oil. Duplicate samples of pastry differed in some cases but in general there was better agreement than in the previous tests. However, a critical judgment could detect a characteristic flavour in all the samples prepared from the linseed oil shortenings.

4. The Effect of Degree of Hardening

In the work reported above the samples of shortening had been hydrogenated to iodine numbers ranging from about 60 to 70. These had melting points in the range of 45 to 50°C. and were definitely too hard to be nicely worked in making pastry. This factor possibly accounted for some of the variability observed between duplicate pastry samples. Nevertheless it had been felt that these samples had a better chance to be free from reversion than ones less completely hydrogenated. A study of this point was considered necessary.

Eight samples of an unrefined hot-pressed linseed oil were hydrogenated with 1.0 per cent of nickel catalyst to iodine numbers ranging from 60 to 90. The actual iodine numbers were: 61, 67, 68, 72, 76, 83, 87 and 89. The samples were deodorized and then used to prepare pastry.

Qualitative judgments indicated that the pastry prepared from the three samples with the lower iodine numbers were of slightly better flavour. In all samples the characteristic

flavour of reversion was detected but it was generally less strong in these samples. The texture of the pastry was, however, best in those samples prepared from the shortenings of iodine numbers 83 and 87. For desirable physical characteristics in mixing the pastry, the shortening with the iodine number of 83 was preferred by the girl who did the baking.

5. Blending a Linseed Oil Shortening with Sunflower Seed Oil

a. Samples tested at Macdonald College

The last experiment had shown that by hydrogenating linseed oil to an iodine number of below 70 the intensity of the reversion flavour in the shortening might be slightly reduced. But since such a shortening was too hard for easy mixing into pastry its use would necessitate softening, by blending with a low melting oil or fat. It was decided to investigate the use of alkali-refined sunflower seed oil for such blending.

Two samples of a hot-pressed alkali-refined and adsorbent-refined (silica gel-alumina) linseed oil were hydrogenated to an iodine number just below 70. (The actual iodine numbers were (a) 67.5, and (b) 69.0). They were then deodorized with steam and filtered, to give shortenings practically free of colour and odour. The samples (a) and (b) were then blended with sunflower seed oil in the following proportions:

(a) two parts linseed oil shortening and one part sunflower seed oil

(b) four parts linseed oil shortening and one part sunflower seed oil.

Both of these blended shortenings were of satisfactory colour and odour and when used in making pastry were considered to be within the range of satisfactory hardness. The pastries were of good texture and qualitative judgments indicated the flavour to be generally good and in a number of the judgments these pastries were considered as good or better than that from Domestic Shortening. There seemed to be less differences between duplicate pastry samples than had been observed before suggesting that hardness of the shortening had been a factor contributing to the differences, but since differences were still noticed, this could not account for it all. The presence of these amounts of sunflower seed oil may have contributed to mask the reversion flavour in these samples, but it did not eliminate it, for this characteristic flavour could still be noticed.

b. Samples tested by the Cereal Division, Central Experimental Farm, Ottawa

Two samples of hydrogenated linseed oil shortening were prepared from an alkali-refined linseed oil. These had iodine numbers (a) 68, (b) 62. Both were of satisfactory colour and odour. A portion of each was blended (as before) with alkali-refined sunflower seed oil in the following proportions:

(a) three parts linseed oil shortening with one part
sunflower seed oil

(b) two parts linseed oil shortening with one part sun-
flower seed oil

The remaining portions of the two original shortenings and the two blended shortenings were sent to the Cereal Division, Central Experimental Farm, Ottawa. They were designated by the following numbers:

- | | |
|--------|------------------|
| (a) 25 | (a) blended 25.1 |
| (b) 26 | (b) blended 26.1 |

The four samples were tested in bread, using 4 per cent shortening in the dough. They were reported on as follows:

"Shortenings Nos. 25 and 26 were too hard to blend properly in the dough and remained in small pieces throughout the mixing and fermentation periods. This inadequate blending was apparent as well in the finished loaf. A slight oily off-taste was observed in the toasted and untoasted bread, although this could be attributed partly to the uneven distribution of the shortenings.

"Shortenings Nos. 25.1 and 26.1 blended satisfactorily into the doughs and produced loaves comparable to the standard in which Domestic Shortening was used. Four persons sampled the fresh bread and toasted slices from the loaves made from these two shortenings and in neither case could they make a distinction between them and the fresh bread and toasted slices from the check loaf."

Later a test of these four shortenings was made with pastry. In this test the reverted flavour could be detected in all samples.

These results with pastry confirm our own findings with the previous samples. The samples sent to the Cereal Division had not been adsorbent refined, but it seems doubtful that this would have brought a much more favourable report since the advantages we had observed for this additional refining were not great. Certainly the reverted flavour would still have been present. It is interesting that these shortenings

proved so satisfactory in bread; however, the small proportion of shortening in the dough must be noticed here.

6. A Study of Different Samples of Linseed Oil with Different Treatments

Seven different samples of linseed oil were obtained by Mr. W.H. Lemon from certain commercial plants. The seven samples are described as follows:

1. Hot-pressed linseed oil from Dominion Linseed Oil Co.Ltd.
2. Cold-pressed " " " " " " "
3. Hot-pressed " " " Toronto Elevator, Ltd.
4. Cold-pressed " " " " " "
5. Hot-pressed " " " Canada Linseed Oil Mills,Ltd.
6. Cold-pressed " " " " " " "

7. Special oil No. 100 from Pittsburgh Plate Glass Co.

The sample No. 7 is the fraction of low iodine number obtained by furfural extraction of linseed oil. This sample has an iodine number of 155.

A sample of about 425 g. of each of these different oils was received by the author. From each sample was taken two portions of 200 g. each. One of these portions was hydrogenated directly. This gave a series of shortenings (numbered 31 to 37 respectively) prepared without any refining prior to hydrogenation. The other of these portions was alkali refined and then hydrogenated. This gave a series of shortenings (numbered 41 to 47 respectively). Each of the hydrogenations was carried out with 1.0 per cent of nickel

catalyst for the unrefined oils and 0.5 per cent of nickel for the alkali-refined oils. The hydrogenations were all at 180°C., and all were continued to give shortenings with iodine numbers of about 65.

In addition to these 14 shortenings prepared from the seven oils, two series of shortenings (duplicates) were prepared by Mr. W.H. Lemon. These samples were alkali-refined and adsorbent-refined and then hydrogenated at 150°C. to iodine numbers of about 75 to 80. Both series of samples were received by the author for tests on flavour reversion. They were numbered 71 to 77 and 81 to 87 respectively for this study.

Thus there were four series of shortenings representing three different treatments, each series containing seven samples. A testing scheme was planned which would give a quantitative evaluation of the quality of these shortenings with regard to flavour reversion. It was hoped that information, of a more definite nature than had been possible with the qualitative tests previously employed might now be obtained regarding the effect of the following factors on flavour reversion:

The difference between hot-pressed and cold-pressed oils.

The difference between samples of hot-pressed oil.

The difference between samples of cold-pressed oil.

The value of alkali refining prior to hydrogenation.

The value of adsorbent refining in addition to alkali refining.

The advantage if any of using the linseed oil fraction of low iodine number.

The testing technique has been described in detail under "Methods". Three separate tests were made with different baked products: (a) muffins, (b) biscuits, (c) pastry. Only twenty-four samples could be studied in one test; the following were selected:

Test (a): samples 31 to 37, 41 to 47, 81 to 87.

Test (b): samples 31 to 37, 41 to 47, 71 to 77.

Test (c): samples 31 to 37, 41 to 47.

This placed twenty-one samples in each of the tests (a) and (b). In test (a) the remaining three samples included were (1) Domestic Shortening, (2) Domestic Shortening hydrogenated to resemble in hardness those linseed shortenings of iodine number about 65, (3) a linseed oil shortening composed of a sample which had been hardened only to an iodine number of 108, blended with a very hard hydrogenated linseed oil with an iodine number of 33. These were blended in the proportions of 2 parts of the soft to 1 part of the hard sample giving a product of satisfactory physical properties. This sample was included to give some further indication of the effect of the extent of hydrogenation on reversion. In test (b) the three additional samples included were all Domestic Shortening. In test (c) the fourteen samples indicated above were studied with eight of another series (to be described in a later section). The remaining two samples were

Domestic Shortening. In tests (a) and (b) the samples were graded on the ten point scale and in the test (c) the samples were rated as acceptable or not acceptable.

The scoring of the samples in each of the tests is shown in Figures 12, 13 and 14. The "Score of Quality" here is the average score given by each group of judges on each sample. The scoring of the "controls" is also shown in these figures. The data were arranged in tabular form and the analyses of variance carried out as shown in Tables I, II and III. Here all scores have been multiplied by 10 to remove decimal points. The samples are described as to oil number (1 to 7) and treatment number (3, 4, 7 or 8); the latter indicating the series (31, etc., 41, etc., 71, etc., and 81, etc.) to which the sample belongs.

The tables and statistical calculations show that the factors controlled in this experiment, viz., the nature of the samples and the refining treatment, do not account for a large part of the variability in judgments of quality. In one test a distinct improvement in quality was indicated with further refining of the oil, but the other two tests did not show this to be a significant factor. When the samples from cold-pressed oils were compared with those from hot-pressed oils, there were found to be no significant differences.

It was observed by the author and a few other judges in a qualitative way, that there were genuine differences in the baked samples as the recorded scores indicated. It was often felt that some of the samples might reasonably be scored as

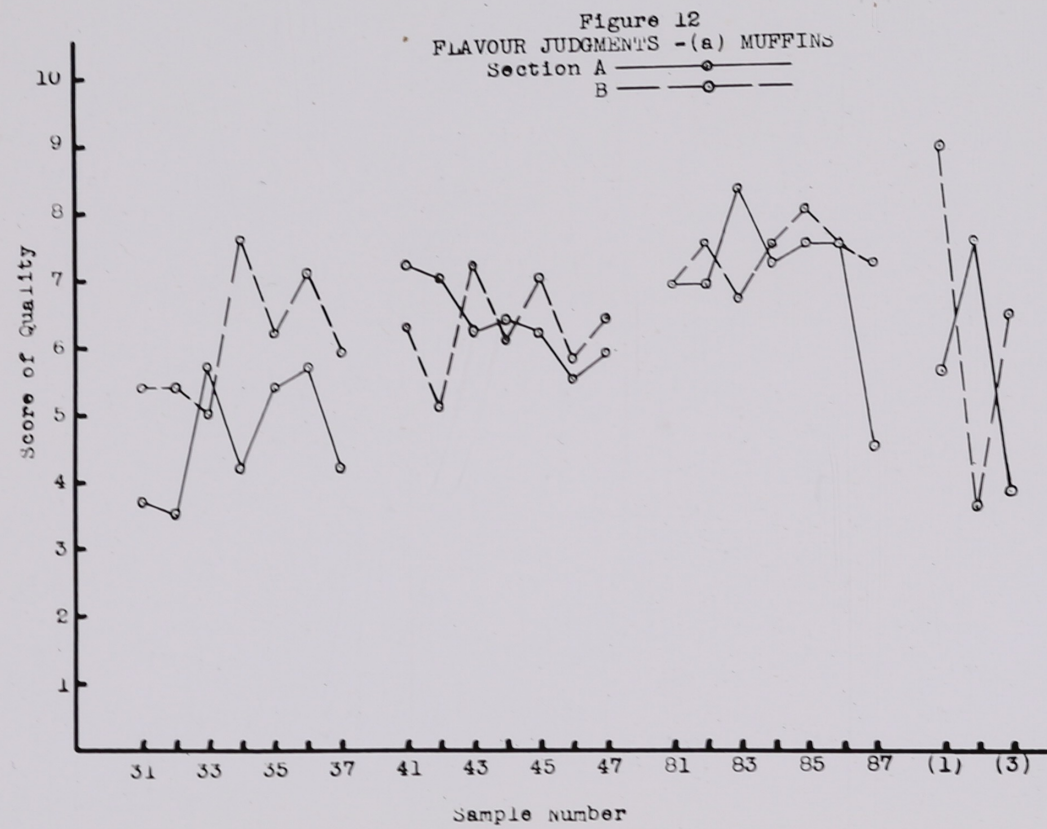


Figure 13
FLAVOUR JUDGMENTS -(b) BISCUITS
Section A ———○—————
B ———○—————

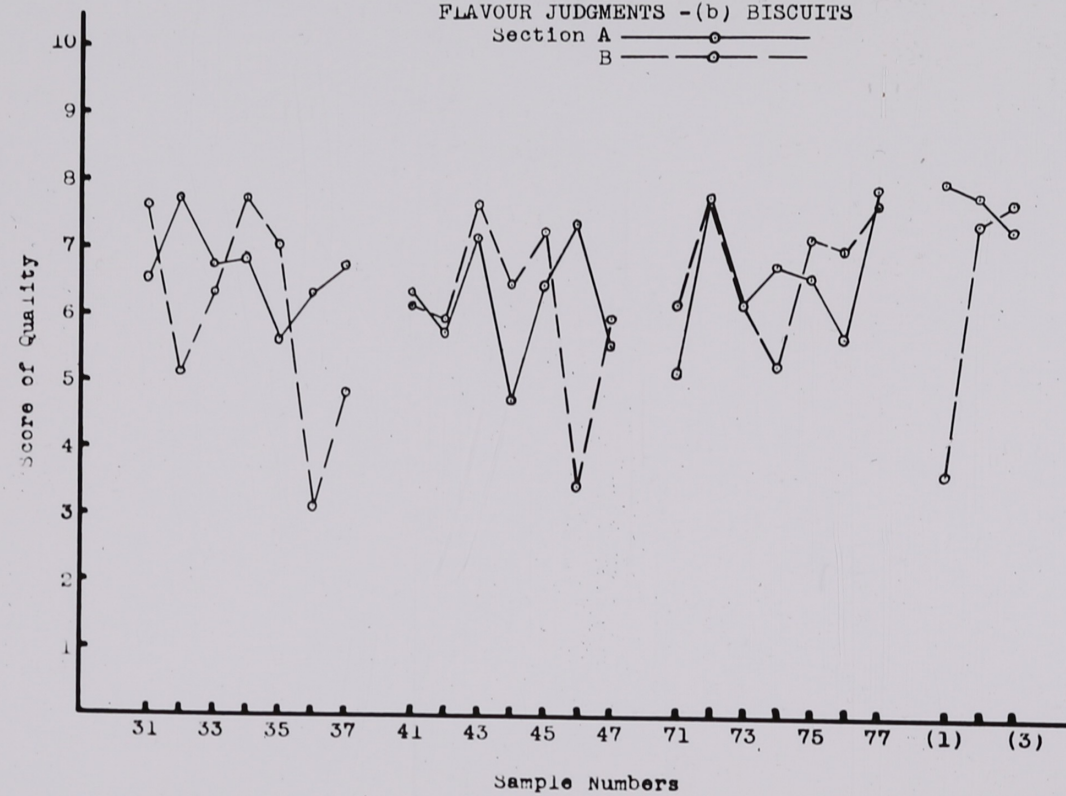


Figure 14
FLAVOUR JUDGMENTS - (c) PASTRY
Section A ———
Section B - - - -

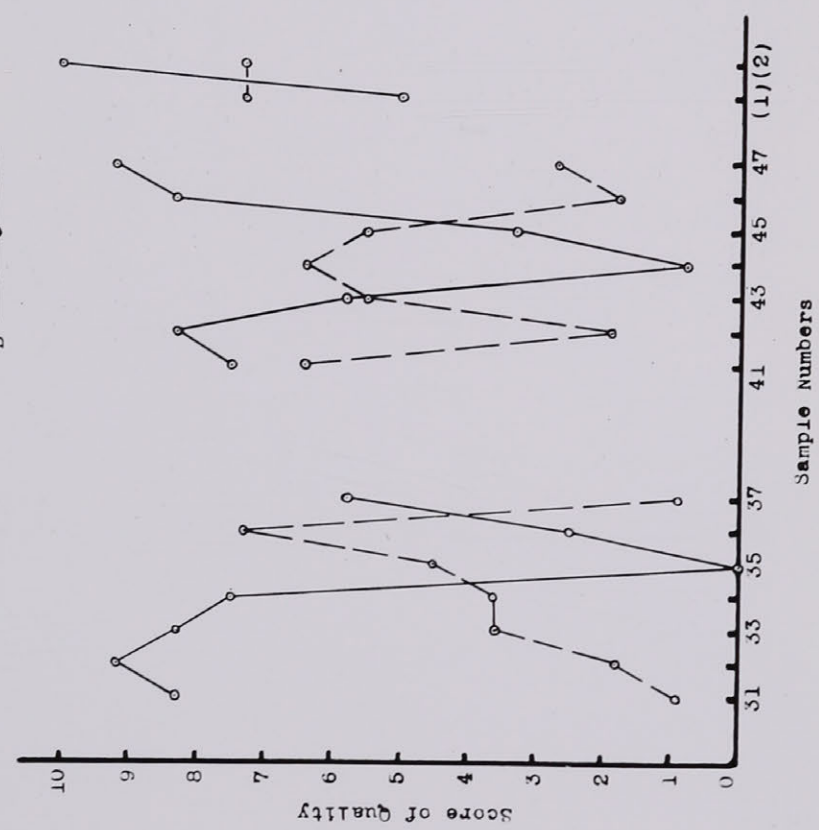


TABLE I

Analysis of Flavour Judgments: (a) Muffins

Treatment	Group A				Group B			
	3	4	8	Totals	3	4	8	Totals
Oil No.								
1	37	72	69	178	54	63	69	186
2	35	70	69	174	54	51	75	180
3	57	62	83	202	50	72	67	189
4	42	64	72	178	76	61	75	212
5	54	62	75	191	62	70	80	212
6	57	55	75	187	71	58	75	204
7	42	59	45	146	59	64	72	195
Totals	324	444	488	1256	426	439	513	1378

<u>Source of Variance</u>	<u>Degree of Freedom</u>	<u>Mean Square</u>
Between samples	6	89.7
Between groups	1	354.0
Between treatments	2	1126.5 ¹
Samples x treatments	12	21.9
Error	20	110.
	41	

1 Surpasses one per cent level of significance. No other factor was significant at the 5 per cent level. The difference between each of the treatments (on the means of the two groups) was significant at the 5 per cent level.

TABLE II

Analysis of Flavour Judgments; (b) Biscuits

Treatment	Group A				Group B			
	3	4	7	Totals	3	4	7	Totals
Oil No								
1	65	63	51	179	76	61	61	198
2	77	57	77	211	51	59	77	187
3	67	71	61	199	63	76	61	200
4	68	47	67	182	77	64	52	193
5	56	64	65	185	70	72	71	213
6	63	73	56	192	31	34	69	134
7	67	55	78	200	48	59	76	183
Totals	463	430	455	1348	416	425	467	1308

<u>Source of Variance</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Between samples	6	110.1
Between groups	1	38.0
Between treatments	2	82.5
Samples x treatments	12	141.6
Error	20	121.5
	41	

No factor was significant at the 5 per cent level.

TABLE III

Analysis of Flavour Judgments; (c) Pastry

Group A				Group B		
Treatment	3	4	Totals	3	4	Totals
Oil No.						
1	83	75	158	09	64	73
2	92	83	175	18	09	27
3	83	58	141	36	55	91
4	75	08	83	36	64	100
5	00	33	33	45	55	100
6	25	83	108	73	18	91
7	58	92	150	09	27	36
Totals	416	432	848	226	292	518

<u>Source of Variance</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Between samples	6	288
Between groups	1	3,889
Between treatments	1	240
Samples x treatments	6	644
Error	13	1,800
	27	

No factor was significant at the 5 per cent level.

high or nearly as high as the Domestic Shortening control. Nevertheless in all of these products the characteristic reverted flavour could be detected.

7. Recovery of Catalyst

The following experiments were carried out to determine whether the nickel catalyst might be reactivated without removing the nickel from the silica gel carrier.

a. Mixed catalysts

A quantity of catalyst which had been used with oils variously refined was washed with Skellysolve B to remove adhering fat. A portion of this material was saved (No. 1). The remainder was heated in a muffle furnace at 600°C. for four hours and then reduced in hydrogen at 500°C. for two hours (No. 2).

b. Catalysts from alkali refined and crude oils

Catalysts from the series of samples 31 to 37 (above) were combined (No. 3) and compared with those from hydrogenation of the samples 41 to 47 (No. 4). These two samples of used catalysts were washed with Skellysolve B, placed in a muffle furnace at 700°C. for seven hours, and then reduced in a combustion tube with hydrogen at 500°C. for two hours.

To test the efficiency of these catalysts they were each used at the level of one per cent nickel to hydrogenate 100 g. of an alkali-refined linseed oil (of iodine number 181). The amount of reduction and time required was as follows:

TABLE IV
Efficiency of Recovered Catalysts

Catalyst Number	Time of Hydrogenation (minutes)	Final Iodine Number
(1)	210	101
(2)	270	90
(3)	70	108
(4)	70	149

These results indicated that only a small part of the original activity of these catalysts had been recovered through these treatments.

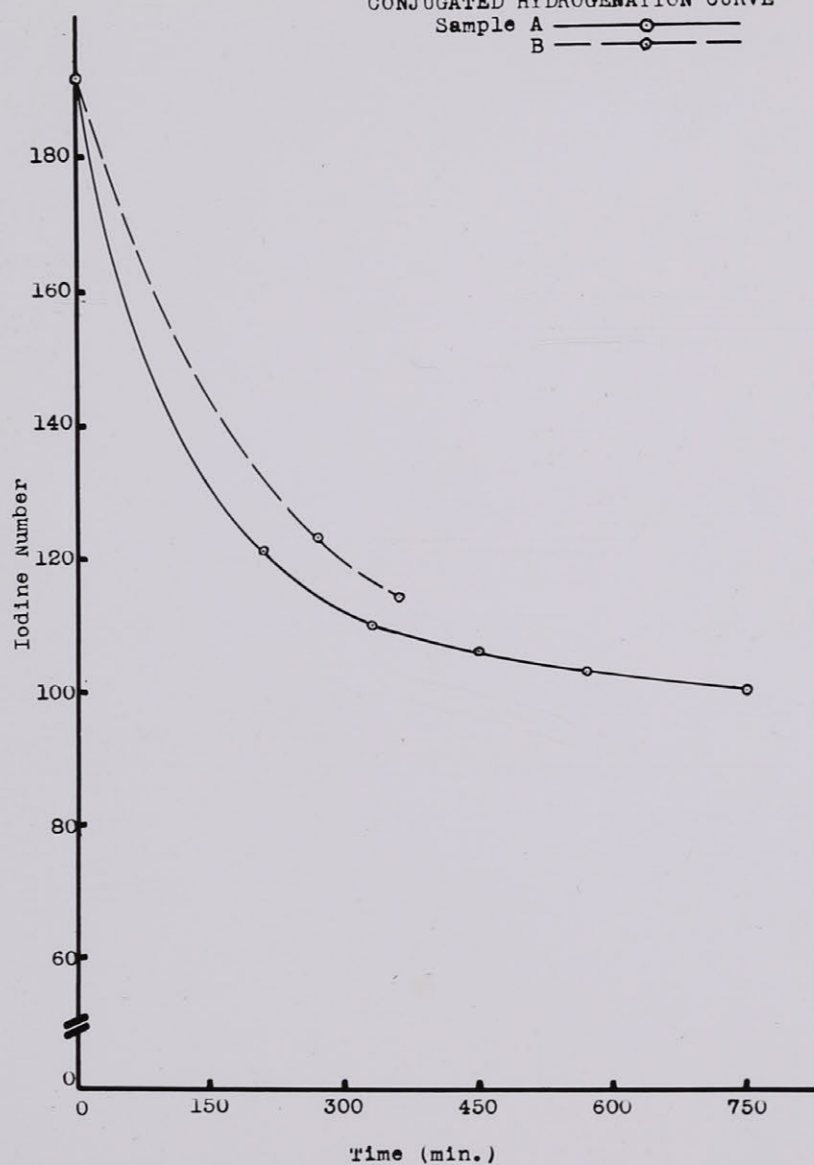
8. Conjugated Hydrogenation

Two experiments were carried out to learn whether or not this type of hydrogenation might result in a product which would be free of reversion. It was also of theoretical interest to know more about the reaction.

Two 100-g. samples of an alkali-refined hot-pressed linseed oil were hydrogenated in the presence of one per cent nickel catalyst at 200°C. while vapours of ethyl alcohol passed continuously through the mixture. In the first experiment, which was allowed to go for twelve hours, 95 per cent alcohol was used and the distillate which collected was passed through again. In the second experiment, which ran only for six hours, vapours from absolute alcohol were passed into the oil-catalyst mixture and the distillate was not returned.

The course of each reaction is shown in Figure 15. It is seen that the use of absolute alcohol did not bring a more

Figure 15
CONJUGATED HYDROGENATION CURVE



rapid reduction of the oil, in fact the 95 per cent alcohol seemed slightly better.

The products from these hydrogenations were soft, but it was possible to test them in making pastry. After deodorizing to remove acetaldehyde, alcohol, etc., the samples were chilled in an ice box. The pastries from both products had definite reverted flavours. They seemed no better than many which had been produced earlier.

B. CAUSES OF REVERSION AND THE USE OF SPECIAL TECHNIQUES

In this section will be described a number of investigations regarding the cause of flavour reversion in linseed oil shortening and a number of experiments using special processes which were suggested by theoretical considerations to offer a means of producing an improved shortening.

1. The Saponifiable and Unsaponifiable Fractions

This experiment was carried out to identify the factor causing reversion with either the saponifiable or the unsaponifiable fraction of linseed oil.

a. Separation of the two fractions

A 500-g. sample of hot-pressed linseed oil was saponified and extracted in 100-g. batches following the procedure described by Hilditch (53 p. 367-9). Each lot of oil was saponified by boiling under a reflux for five hours with 25 g. of potassium hydroxide in 500 g. of 95 per cent ethyl alcohol. Any material not saponified in this treatment was separated in

a continuous extractor and subjected to a further saponification treatment similar to that given to each 100-g. portion of the oil. The unsaponifiable matter was then extracted with diethyl ether during forty-eight hours of continuous extraction, the solution dried by passing it through anhydrous sodium sulphate and the ether was distilled off under a reduced pressure. The residue was freed of the last traces of ether in a vacuum desiccator.

The alcohol-water solution of the saponified matter was distilled in portions under a vacuum to reduce its volume. The distillations were continued to the point where foaming became troublesome when combined residues amounted to ten liters of solution. The fatty acids were freed by treating this solution at 60°C. with an excess of sulphuric acid and stirring by bubbling carbon dioxide through it. Then it was allowed to stand overnight and the free fatty acids in part decanted off and the remainder obtained by washing with diethyl ether. The fatty acids were combined in an ether solution, dried by passing through anhydrous sodium sulphate and the ether removed by distillation under vacuum at 50°C. and finally in a vacuum desiccator.

b. Studies on the unsaponifiable fraction

To determine whether or not the isolated unsaponifiable fraction was responsible for production of the reverted flavour the following samples of shortening were prepared:

- (1) A 100-g. sample of alkali-refined sunflower seed oil was hydrogenated and deodorized.

- (2) A 100-g. sample of the same alkali-refined sunflower seed oil containing one-fifth of the unsaponifiable matter obtained above (i.e. the amount present in 100 g. of linseed oil) was hydrogenated and deodorized.
- (3) A 100-g. sample of Domestic Shortening without treatment.
- (4) A 100-g. sample of Domestic Shortening containing another one-fifth of the unsaponifiable matter obtained above.

These four samples were tested for flavour reversion by preparing pastry. The pastries from the sunflower seed oil shortenings could be distinguished from the others but the flavour was definitely pleasant. Both samples containing the linseed oil unsaponifiable fraction had the same flavour as their controls. No suggestion of the characteristic reverted flavour of linseed oil was noticed by the author or any one of five other judges in these samples.

c. Studies on the fat acid fraction

The following experiment was carried out to learn whether the component responsible for the flavour reversion existed in the fat acids of linseed oil.

The method of Garner (45) was used to re-esterify a portion of the fat acids. A mixture of 200-g. of the fat acids and 25.0 g. (7.3 per cent excess) of glycerol were heated together for six hours at 200°C. in a 500-cc. round-bottom flask while the mixture was stirred vigorously with a

mechanical stirrer and carbon dioxide was bubbled through. A determination of the free-fatty acids remaining showed that 85 per cent had been esterified. The remainder were removed by alkali refining. The resulting neutral oil had a slightly lower iodine number than the original oil (173.5 compared with 176) and was more reddish in colour. It was hydrogenated to an iodine number of 86 and deodorized. The resulting shortening had only a slight colour and odour. Samples of pastry prepared from it had a strong reverted flavour. They were worse than many of the samples which had been prepared from linseed oil directly.

It seemed to be shown definitely by these experiments that a component of the linseed oil fatty acids was responsible for the phenomenon of reversion.

2. Free Fatty Acids

The temperatures employed in processing (180°C . for hydrogenating and 200°C . for deodorizing) could have caused the splitting-off of some free fat acids from the glycerides. It seemed that these might have a part in producing the reverted flavour. This hypothesis was strengthened when a very small sample of the mixed fat acids isolated from linseed oil (above) was tasted. An intense burning sensation was produced at the back of the mouth.

a. Effect of treatment on free fat acid content and on flavour

It had been our practice to determine the content of free fat acids only on crude oils and on the same after refining

to be sure that the refining had been adequate. In this experiment a sample of hot-pressed linseed oil was alkali-refined, hydrogenated and deodorized, and the free fat acid content determined following each treatment. The sample was divided into two portions for hydrogenation so that duplicates were studied in regard to the effect of the latter two treatments. Then, to study the effect of the small amount of free fat acid present on the flavour, one half of each shortening sample was alkali-refined again, and the other half kept as a control on this treatment. The free fat acid content of the samples following these treatments is shown in Table V.

TABLE V
Acid Value at Different Stages in Processing

Description of Sample	Acid Value (per cent Oleic Acid)	
Unrefined	0.81	
After alkali refining	0.034	
After hydrogenating	0.056	0.063
After deodorizing	0.10	0.18
After the second alkali refining	0.028	0.031

To determine the effect of the presence of this amount of free fat acids in the shortening the four samples were tested in making pastry. Qualitative tests of the flavour

did not indicate any superiority for those samples which had the lower fatty acid content. All samples showed the characteristic reverted flavour.

b. Effect of a high concentration of free fat acids

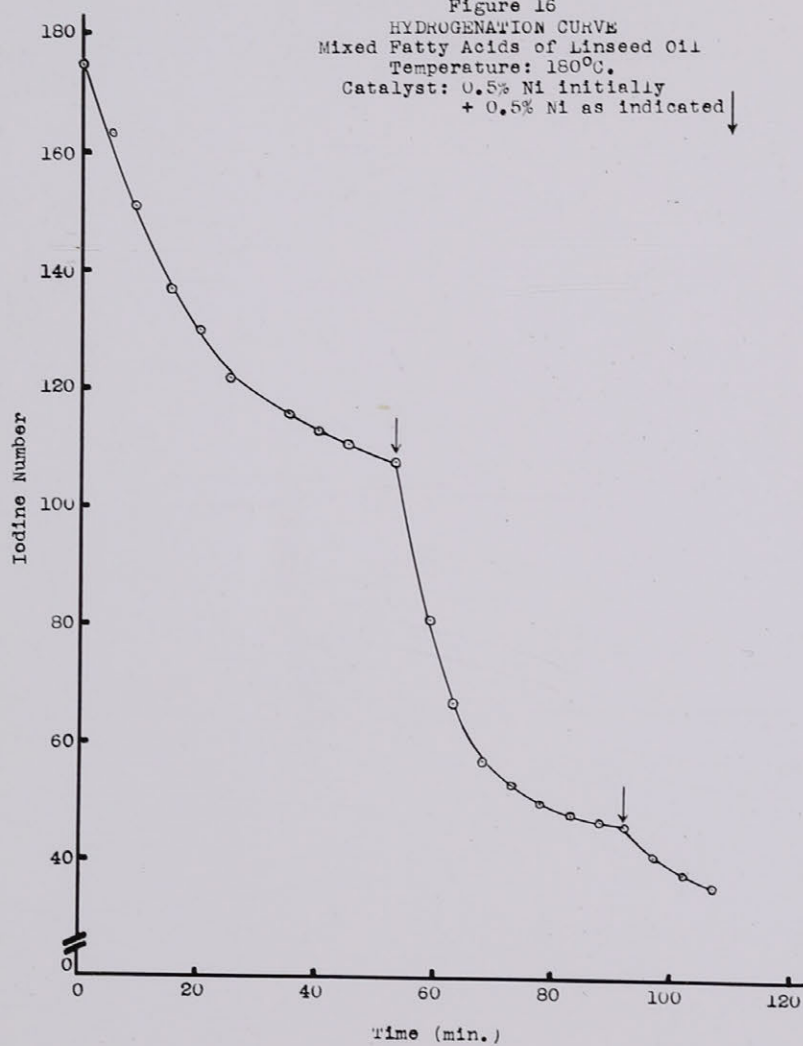
To determine the effect of a large amount of the free fat acids of linseed oil in a shortening, a portion of the fat acids isolated above was hydrogenated until quite hard (iodine number 43), and deodorized. The course of this hydrogenation is shown in Figure 16. One portion of this product was blended with sunflower seed oil (1:1) to give a shortening of suitable physical properties. Then both of these products were tested in making pastry. The flavour of the product prepared from the pure fat acids was the most disagreeable that had been found in any of the products tested, but its flavour was of a different kind. The other product had a pleasant taste when first placed in the mouth, but after a few minutes it caused a very unpleasant irritation at the back of the mouth. The flavour was of the same kind as that from the first sample; it was not like the usual reverted flavour associated with linseed oil shortenings.

It appeared from these tests that the content of free fatty acids was not the important factor in causing reversion flavours.

3. Linolenic Acid

To determine whether linolenic acid was the fatty acid responsible for reversion, a sample of ethyl linolenate was

Figure 16
HYDROGENATION CURVE
Mixed Fatty Acids of Linseed Oil
Temperature: 180°C.
Catalyst: 0.5% Ni initially
+ 0.5% Ni as indicated ↓



prepared. The method of McCutcheon (76) was followed in detail except that saponification was carried out with alcoholic potassium hydroxide (82 p.30b). The pure product distilled at 194°C . at a pressure of 5.5 mm., and had a pale straw colour. It was added to a sample of refined sunflower seed oil so that linolenic acid would be present in about the same proportion as it is in linseed oil: 40 g. ethyl linolenate with 60 g. sunflower seed oil. This mixture was hydrogenated to an iodine number of 75 and deodorized. Pastry made from this shortening had the characteristic flavour of a linseed oil shortening but the flavour was less strong than in many of these samples, probably because of the different flavour of the sunflower seed oil masking the reverted flavour. It was felt that this experiment had demonstrated linolenic acid to be responsible for flavour reversion.

To determine whether hydrogenation was necessary to cause this flavour to develop from linolenic acid, a sample of ethyl linolenate was blended with a sunflower seed oil shortening, again this was done so the mixture would have about 40 per cent linolenic acid. The resulting shortening, used directly, made a pastry which had a strong repulsive flavour; it was different from the characteristic reverted flavour, and much more unpleasant. It was considered from this experiment that although linolenic acid was fundamentally responsible for flavour reversion, nevertheless, hydrogenation brought about a change in it producing the substance which is directly

responsible for the characteristic flavour.

4. Isomerization

The following experiments were carried out to determine whether a relatively simple isomerization of the fat acids might effect an improvement in flavour. The use of prolonged heating at a higher temperature both with and without common isomerization reagents was investigated. Three samples of alkali-refined hot-pressed linseed oil were hydrogenated somewhat less than usual for these tests and were then deodorized. The iodine numbers of the samples for the tests (a), (b) and (c) were respectively 87, 82 and 102.

The tests were as follows:

(a) The sample of hydrogenated linseed oil was heated at 230°C. for 12 hours in the hydrogenation apparatus and the oil was continuously agitated throughout the period. The air in the bottle was flushed out and replaced by hydrogen at a pressure of about five pounds per square inch and no absorption of hydrogen was observed. At the end of the period the hydrogenated oil was again deodorized.

(b) This sample was heated at 230 to 240°C. for six hours while sulphur dioxide was bubbled through it at a rate sufficient to keep the sample agitated. This treatment was followed by deodorization.

(c) This sample was heated at 230 to 240°C. for six hours with one per cent selenium using a mechanical stirrer to agitate the mixture. At the conclusion of the treatment the sample

was filtered and deodorized.

The deodorized shortenings thus obtained had satisfactory odours and colours. The reactions had not caused as much hardening as had been expected so that the sample from test (c) remained somewhat too soft. All samples of pastry had the characteristic reverted flavour and no improvement seemed indicated. Better samples had been produced in some of the previous tests.

5. Effect of Oxidation

To study the effect of oxidation both before and after hydrogenation the following experiments were carried out.

(a) A sample of alkali-refined linseed oil was submitted to a mild oxidation by heating for twelve hours at 98 to 100°C. while air was blown through at a rate sufficient to agitate it. Many off odours were noticed during the course of this treatment but none which resembled that characteristic of reversion in a shortening. The oil was only slightly thickened at the end of the period. The sample was then hydrogenated to an iodine number of 71, and deodorized. The deodorization was continued for five hours but the sample could not be freed of a peculiar and unpleasant odour. It had also a darker colour than the usual samples.

(b) A sample of alkali-refined linseed oil was hydrogenated to an iodine number of 69.5. This was deodorized, and then divided into two parts and each oxidized by blowing air through it under the following conditions:

(1) at 150 - 160°C. for six hours

(2) at 180 - 190°C. for eight hours.

Citric acid (0.1 per cent) was added (104) to remove traces of metals (copper, iron and nickel). These samples were deodorized for five hours giving products free of colour and having only very slight odour.

The three samples were then tested in making pastry. The sample from test (a) had a flavour which was as bad as that in the product from the hydrogenated free fatty acids (above) and in the presence of this strong and repulsive flavour the usual reverted flavour was not noticed. The samples from test (b) had the usual reverted flavour and it seemed no less intense than had been observed in many other samples.

6. The Relation of Oxidation to Reversion

Some studies are described here which were designed to investigate the theory that reversion in linseed oil shortenings is an oxidation phenomenon. The development of the reverted flavour in pastries prepared from these shortenings offered no opportunity to follow the course of the change. However, the development of a reverted odour could be detected in the shortenings themselves when they were heated at 100°C. for a period to bring on this change. As this method offered a means of following the development of peroxide oxidation products at the same time, it was adopted in these studies.

To obtain a quantitative measure of the extent of reversion

ion the techniques described under "Methods" were employed. The test of the judges' accuracy was made by preparing a series of samples of a definitely reverted linseed oil shortening, blended with varying amounts of paraffin wax, to form a graduated scale of intensities of reverted odour. These samples were placed in the Syracuse dishes, a number of each being provided so that in all 31 samples were offered to the panel for judgment. Each sample was scored for intensity of odour on a ten point scale by each of the judges. At the conclusion of the judging the difference (d) between each score given and the true score was determined, this difference was squared (d^2) and the sum of these ($\sum d^2$) for each judge was taken for the calculations indicated below:

TABLE VI
Test of Judges on Panel

Judge Number	$\sum d^2$	$\frac{\sum d^2}{n}$	$F = \frac{\frac{\sum d^2}{n}}{\sigma}$
1	150	5.0	0.746
2	210	7.0	1.045
3	243	8.1	1.211
4	253	8.4	1.255
5	319	10.6	1.58
6	106	3.5	0.522
7	158	5.3	0.791
8	288	9.6	1.432
9	142	4.7	0.702
10	157	5.2	0.776
11	126	4.2	0.627
12	259	8.6	1.283
Total	2411		

$n = \text{number of degrees of freedom} = 31-1 = 30$

$$\text{Standard deviation} = \frac{\text{total } \sum d^2}{n \times 12} = 6.70$$

F value ($P = 0.05$, $n_1 = 30$, $n_2 = 360$) = 1.47

Only in one case (Judge No. 5) was F greater than 1.47 and since the value of P was taken at the 5 per cent level it was considered that all of the judges should be retained in the panel.

a. Changes at ten-hour intervals

The first experiment studied the twenty-eight samples of shortening prepared from the seven different oils and included the three controls from the baking test (a). A measurement of the peroxide content and of the odour of each of these samples was taken initially and after 10, 20, 30 and 40 hours of heating at 100°C. The change in each factor (peroxide and odour) which had occurred from the beginning of the test was calculated for each period of heating and expressed as a rate of change per hour. These are indicated in Table VII. The odour judgments were expressed by the judges on the ten-point scale and the change here reported represents a decrease in quality. The control samples are labelled

- (1) Domestic Shortening.
- (2) Domestic Shortening hardened.
- (3) Mixture of very hard and very soft linseed oil shortenings.

The values obtained at forty hours are not shown since in a number of cases the peroxide content had decreased from that at thirty hours and thus could not be compared with the others.

TABLE VII

Relation of Peroxide Content to Reverted Odour

Sample No.	Rate of change of odour during heating period of			Rate of change in peroxide content during heating period of		
	10 hr.	20 hr.	30 hr.	10 hr.	20 hr.	30 hr.
31	0.24	0.13	.12	1.11	9.22	44.7
32	.38	.17	.14	7.26	16.45	46.7
33	.09	.11	.11	0.01	0.09	4.6
34	.15	.13	.13	0.05	5.83	19.7
35	.26	.15	.13	0.53	7.28	27.5
36	.30	.19	.16	11.37	25.23	30.8
37	.22	.19	.13	13.22	21.36	34.6
41	.27	.14	.12	4.40	12.67	28.4
42	.08	.06	.09	12.52	24.31	17.8
43	.25	.17	.15	11.04	20.96	26.2
44	.01	.07	.07	0.02	0.06	4.7
45	.19	.16	.14	8.04	16.62	4.5
46	.20	.16	.12	0.20	7.89	16.1
47	.25	.17	.12	20.08	22.04	31.5
71	.27	.14	.13	1.25	3.08	14.7
72	.20	.11	.12	2.83	5.08	14.6
73	.17	.14	.11	2.93	5.41	16.8
74	.25	.15	.08	4.25	8.15	13.8
75	.19	.12	.11	0.85	1.52	40.3
76	.24	.17	.14	4.48	7.51	23.9
77	.24	.18	.17	4.04	10.08	23.9
81	.26	.11	.14	1.98	4.54	19.8
82	.27	.15	.14	5.70	14.73	37.6
83	.25	.19	.15	3.82	8.74	30.3
84	.20	.16	.17	4.63	9.09	23.9
85	.17	.16	.12	1.40	2.61	13.6
86	.18	.13	.11	1.20	3.01	16.0
87	.20	.15	.15	2.16	6.43	19.3
(1)	.15	.16	.16	35.92	37.21	27.8
(2)	.16	.17	.13	6.21	10.23	11.3
(3)	.00	.00	.04	2.05	11.86	38.2

This decrease is attributed to peroxides in the fat breaking down more rapidly than they are formed at this stage of the oxidation.

To obtain a quantitative estimate of the extent of the relationship between development of odour and increase in peroxide, the coefficients of correlation between the rates of change of these two factors for each of the first three periods were calculated (omitting the three "control" samples). The results were as follows:

<u>Length of heating period</u>	<u>Correlation coefficient</u>
10 hours	0.22
20 hours	0.35
30 hours	0.35

Since these values were less than required for significance, these data did not indicate the development of peroxides to be an important factor in the development of odour.

The results of this experiment, however, could not be considered as conclusive since for two reasons the data obtained may not have accurately shown the changes taking place. First, the heating periods (ten hours) were such as to allow relatively large changes to occur between the time of taking one sample and the next. Second, it was necessary with this number of samples to leave them out of the oven for two days to complete the peroxide determinations and prepare the apparatus and reagents for the next determinations. There

may have been changes occurring during this time (68 p.137) that would differ in extent between the samples and of which no measure was made.

b. Changes at two-hour intervals

Two samples of hydrogenated linseed oil shortening were prepared, one (No. 1) from the unrefined oil and the other (No. 2) from the oil after alkali-refining, having iodine numbers of 74 and 64 respectively. Samples of each were placed in twenty Syracuse dishes. Two of the samples of each shortening were placed in the oven at 100°C. at each two hour interval throughout one day. At midnight all dishes were taken out of the oven, samples for peroxide determination weighed into flasks and placed at a temperature of 5°C. until the next morning when these determinations were completed. By this means data were obtained on duplicate samples of each shortening which had been in the oven continuously for 2, 4, 6.....20 hours, and on the controls which had not been in the oven. These data are shown graphically in Figures 17 and 18. The scores for extent of reverted odour are the percentages of the judgments which indicated each sample to be reverted. In the figures the lines are drawn through the means for the duplicate samples.

In all the following tests of reversion odour the samples were kept continuously in the oven for the periods indicated, and judgments of odour were given in the manner used here.

These results indicate more clearly than those from the

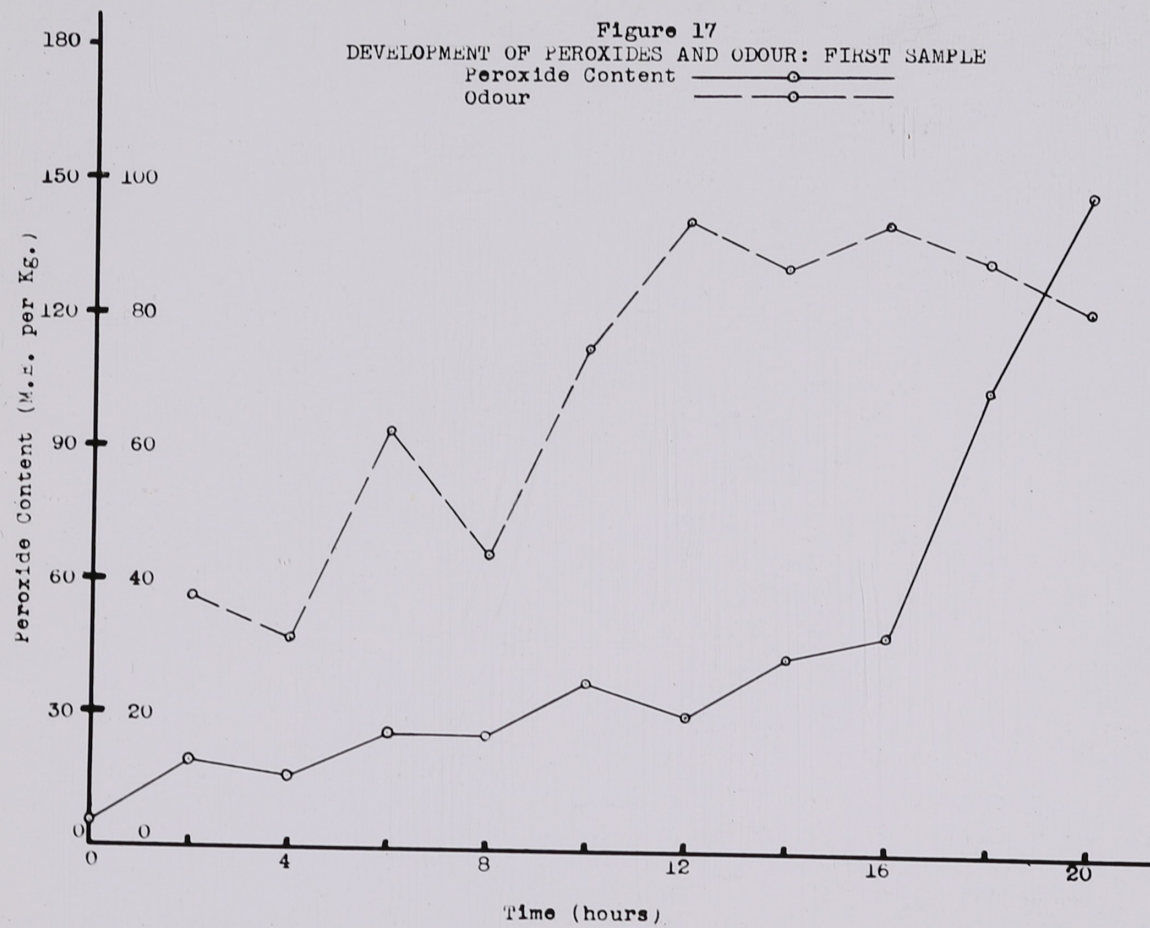
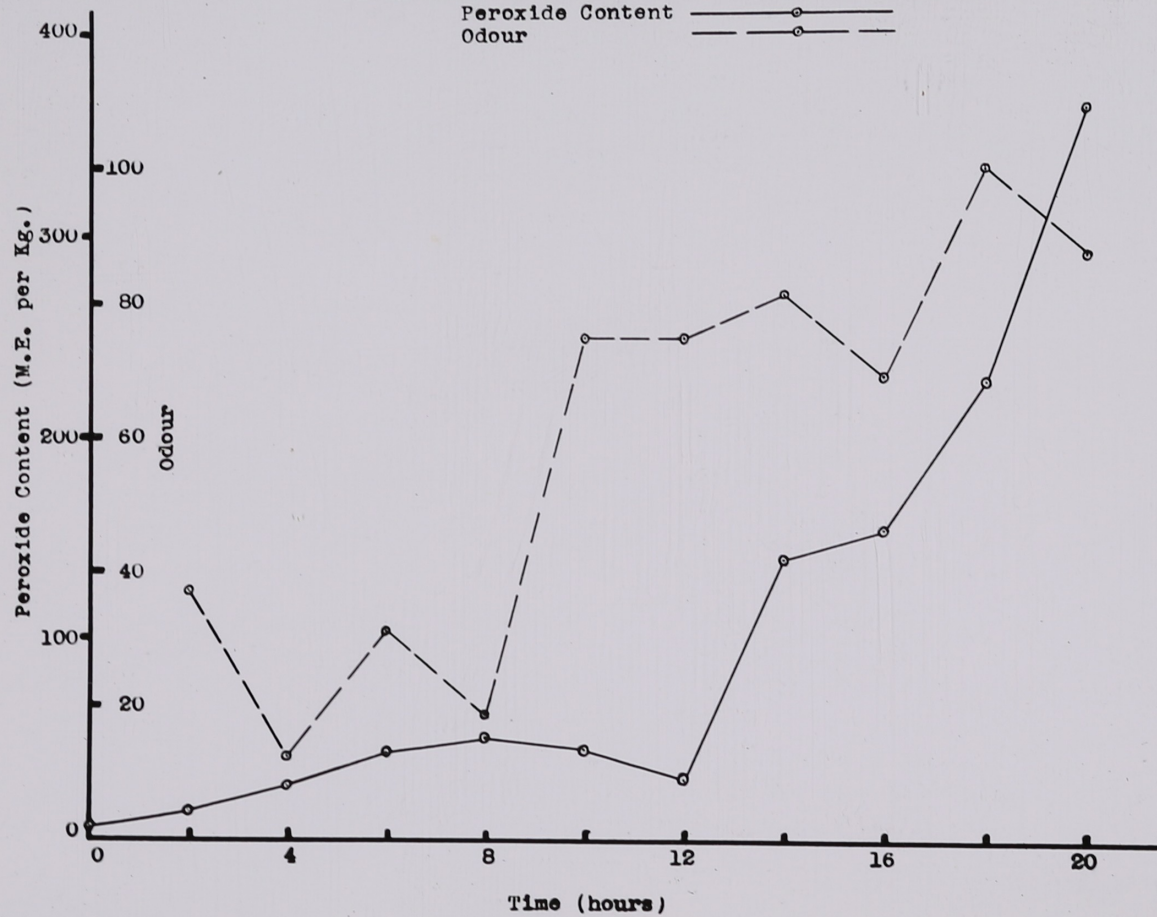


Figure 18
DEVELOPMENT OF PEROXIDES AND ODOUR: SECOND SAMPLE
Peroxide Content ———○—————
Odour ———○—————



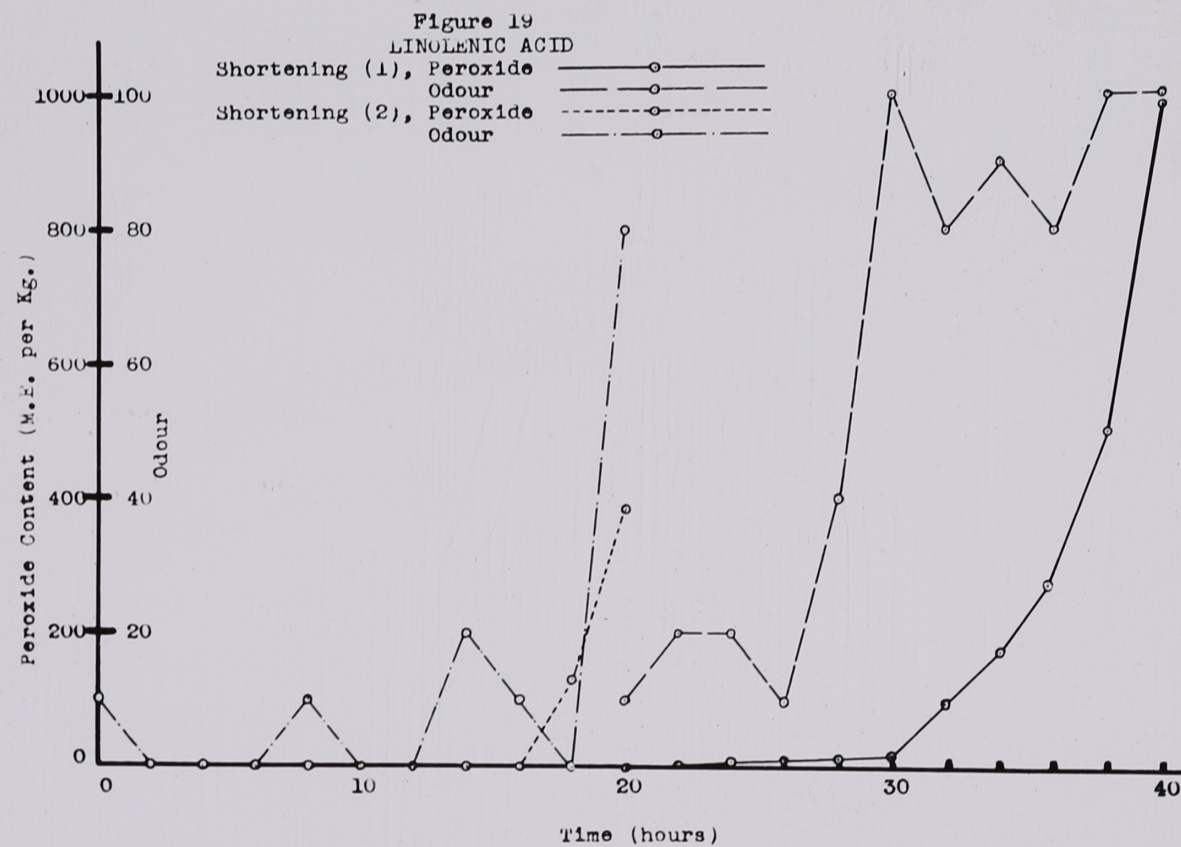
last experiment that a relation exists between the development of the reversion odour and the formation of peroxide compounds in the fat. Reversion would seem to occur shortly before the peroxide content increases sharply.

c. Studies with Ethyl Linolenate

A portion of the shortening prepared above by hydrogenating the mixture of sunflower seed oil and ethyl linolenate was studied as in the last experiment and a shortening prepared from pure sunflower seed oil (iodine number 64) was studied at the same time for comparison. These were designated (No. 1) and (No. 2) respectively. Samples of each shortening were heated for intervals up to twenty hours. It was found, however, that only (No. 2) had increased appreciably in peroxide content; the mixed shortening showed no change in odour and no development of peroxides, so these samples were all returned to the oven for a further twenty hours. After this second heating a number of the samples had the odour characteristic of a reverted linseed oil shortening and also had high peroxide contents. The results are shown graphically in Figure 19. The odour judgments were made on the samples of the pure sunflower seed oil shortening heated for 0 to 20 hours and on the mixed shortening samples which had been heated from 20 to 40 hours.

7. Fractionation With Acetone

In this experiment it was sought to investigate the possibility of removing from linseed oil shortening a fraction



responsible for reversion. Fractionation of the shortening was effected by crystallization from acetone following the general description given by Hilditch (53 p.412-13). The acetone used was carefully dried and twice distilled as for the peroxide determinations. Three shortenings were studied which had been prepared from alkali-refined linseed oil and had iodine numbers of 83, 65 and 54 respectively.

A 300 cc. portion of acetone was added to 60 g. of each shortening and the mixture was warmed to about 50°C. until solution was complete, then the solution was placed outside for 2 days at a temperature between -5 and -10°C. The fat that had crystallized from solution was separated on a "Buchner funnel with suction and the "cake" pressed to remove acetone as completely as possible. This fraction was again dissolved in 300 cc. warm acetone and allowed to stand at room temperature until the next day. Again the insoluble portion was filtered off. The two filtrate fractions were evaporated on a water bath yielding two fractions of increasing solubility and the last traces of acetone were removed in a vacuum desiccator. The amount and iodine number of each fraction are indicated in Table VIII. The fractions are designated:

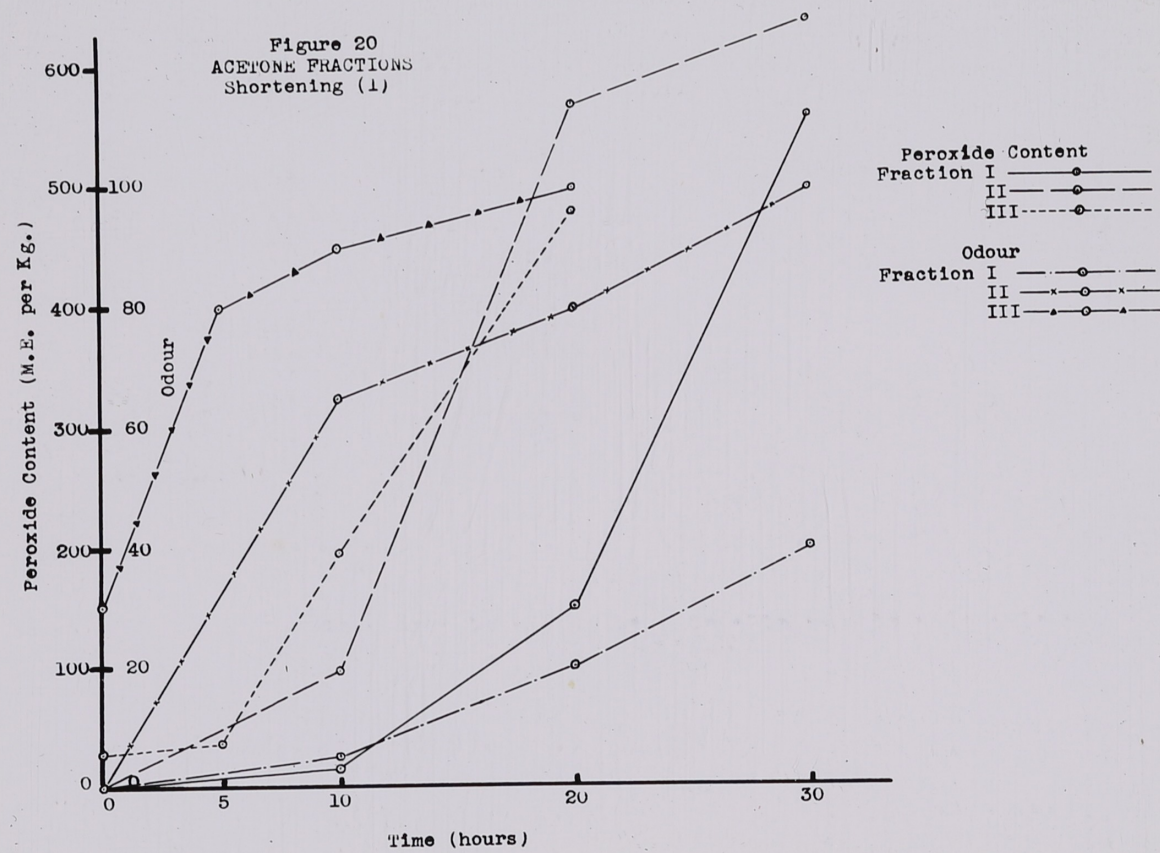
- I. (hardest) crystallized from solution at room temperature.
- II. (middle) was soluble at room temperature but crystallized from solution in the cold.
- III. (softest) was soluble even in the cold.

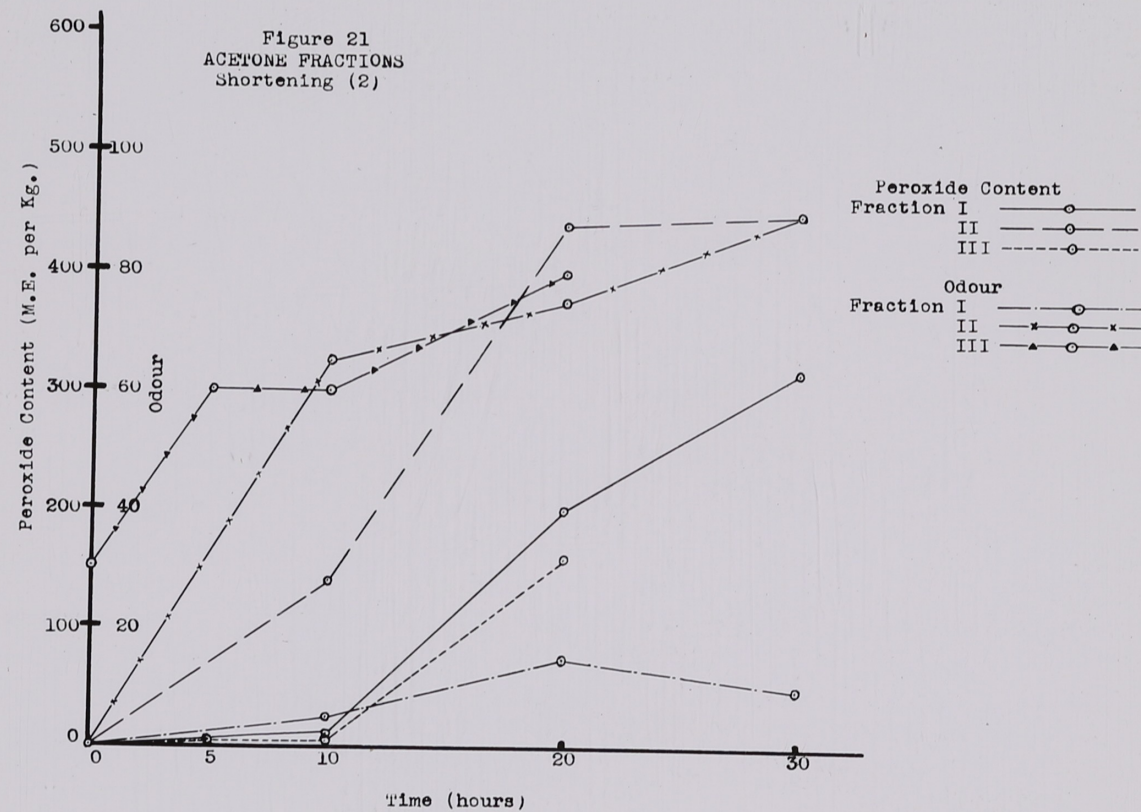
TABLE VIII

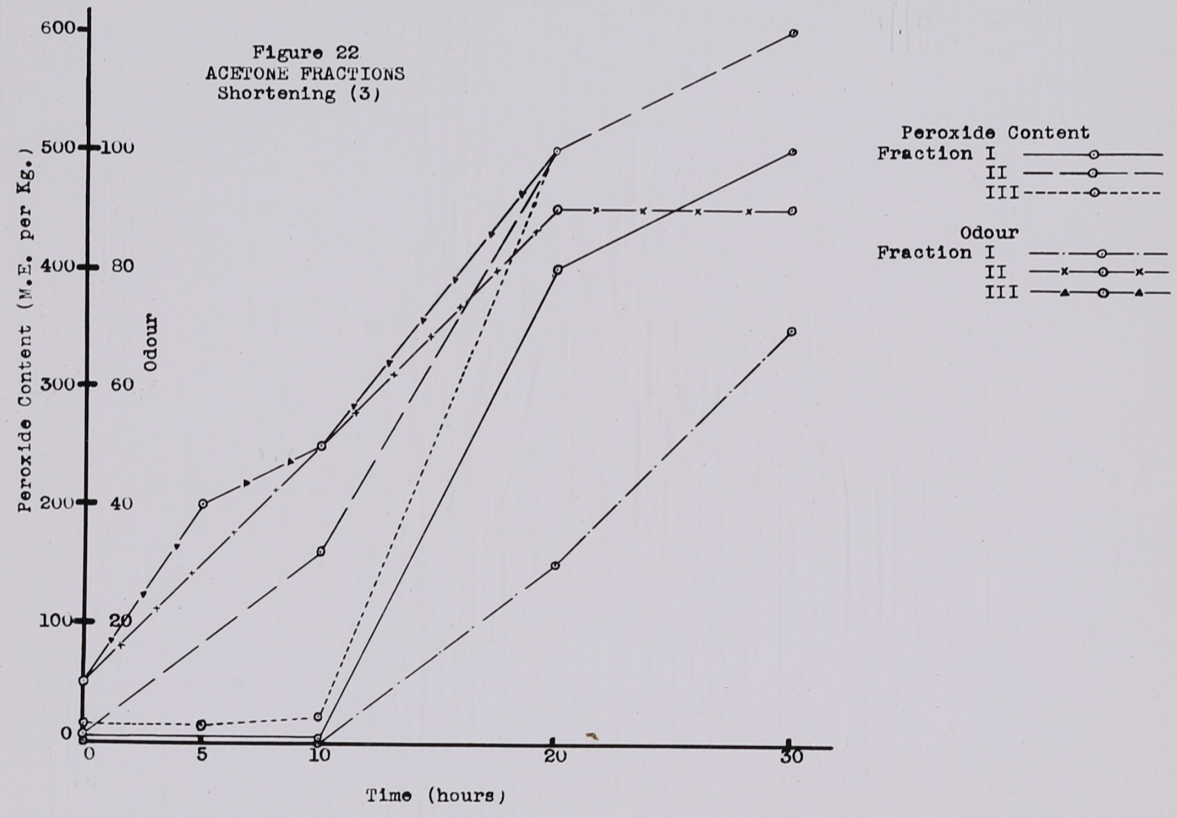
Acetone-Crystallized Fractions

Shortening number	Fraction number	Per cent of whole sample	Iodine number
(1)	I	14.0	58.
	II	58.7	86.
	III	27.3	112.
(2)	I	39.8	46.
	II	45.6	81.
	III	14.8	95.
(3)	I	55.0	39.
	II	33.8	74.
	III	11.3	87.

The increases in reversion odour and peroxide content in all fractions were determined after heating in the oven at 100°C. In the case of the softest fraction the heating periods were 5, 10 and 20 hours for the two harder fractions the periods were 10, 20 and 30 hours. The data are shown in Figures 20, 21 and 22.







8. The use of Antioxidants

The existence of a close relationship between reversion and oxidation in the linseed oil shortenings had not been shown conclusively in the preceding experiments but some relationship had been indicated. Tests with antioxidants seemed to offer another approach to this study. The ability of antioxidants to retard the formation of peroxides in fats is well known. The following experiments were planned to see whether or not they might at the same time retard or prevent reversion in these shortenings. If they should prove to have this ability, a means of making linseed oil shortening a satisfactory edible material might at the same time be discovered.

Two materials served as the basic antioxidants studied:

- (1) "Formula C", which is 65 per cent wheat germ oil, 30 per cent crude soybean lecithin and 5 per cent citric acid.
- (2) Derivatives of gallic acid: isopropyl gallate and glycerol gallate.

The latter were prepared as described by Christiansen (26). The crude preparation before final recrystallization was used.

These antioxidant materials have been used singly at various levels, in combination with each other and with various additional substances in smaller amounts. Tests of reversion have been made both by observing the development of the reversion odour in the shortenings after heating at 100°C., and by baking tests with pastry.

a. Addition of Formula C in processing a shortening

Formula C was added at the level of 0.1 per cent to four samples of linseed oil at different stages in processing them to produce a shortening. In addition, three samples had hydroquinone added at a level of 0.02 per cent, also at different stages. The points in the process at which the additions were made are indicated in Table IX. These samples were prepared by Mr. W.H. Lemon and a control sample of linseed oil shortening to which no antioxidant had been added was also supplied.

(1) Baking test. These shortenings were used in making pastry as part of the third test conducted on the shortening samples prepared from the seven different oils (cf. p.77) and the samples in this experiment were randomized with the other samples in that baking test. The results of this test are shown in Table IX.

TABLE IX

Formula C Added in Processing

Sample No.	Antioxidant used and stage at which it was added	S c o r e s		
		Section A	B	Totals
1	Control - no antioxidant	5.8	6.4	12.2
2	Formula C before bleaching	8.3	0.0	8.3
3	Formula C before hydrogenating	9.2	4.5	13.7
4	Formula C before deodorizing	0.8	6.4	7.2
5	Formula C after deodorizing	9.2	9.1	18.3
6	Hydroquinone before bleaching	5.8	6.4	12.2
7	Hydroquinone before hydrogenating	8.3	8.2	16.5
8.	Hydroquinone after deodorizing	8.3	6.4	14.7
(1)	Domestic Shortening	5.0	7.3	12.3
(2)	Domestic Shortening	10.0	7.3	17.3

(2) Reversion odour and peroxides. The control sample of linseed oil shortening and those having Formula C were studied further for relationship between peroxide formation and development of the reverted odour. The results are shown in Figures 23 and 24. Both the baking test and the test of odour development show that the addition of Formula C after deodorizing brought a marked stability to reversion (as well as to peroxide formation in the last test).

b. Formula C at different levels

A sample of alkali-refined linseed oil shortening of iodine number 68 was prepared. It was divided into six portions, one of which served as a control while Formula C and other antioxidants were added as indicated in Table X.

TABLE X

Formula C at Different Levels

Sample Number	Percentage of each antioxidant added					
	1	2	3	4	5	6
Antioxidant added:						
Formula C		0.01	0.01	0.1	0.1	
Isopropyl gallate			0.0025		0.025	
Licithin						0.00200
Gallic acid						0.00050
Citric acid						0.00025
Glycerol gallate						0.00725
Vitamin E						0.00050
Total antioxidant(%)	0.0	0.01	0.0125	0.1	0.125	0.01050

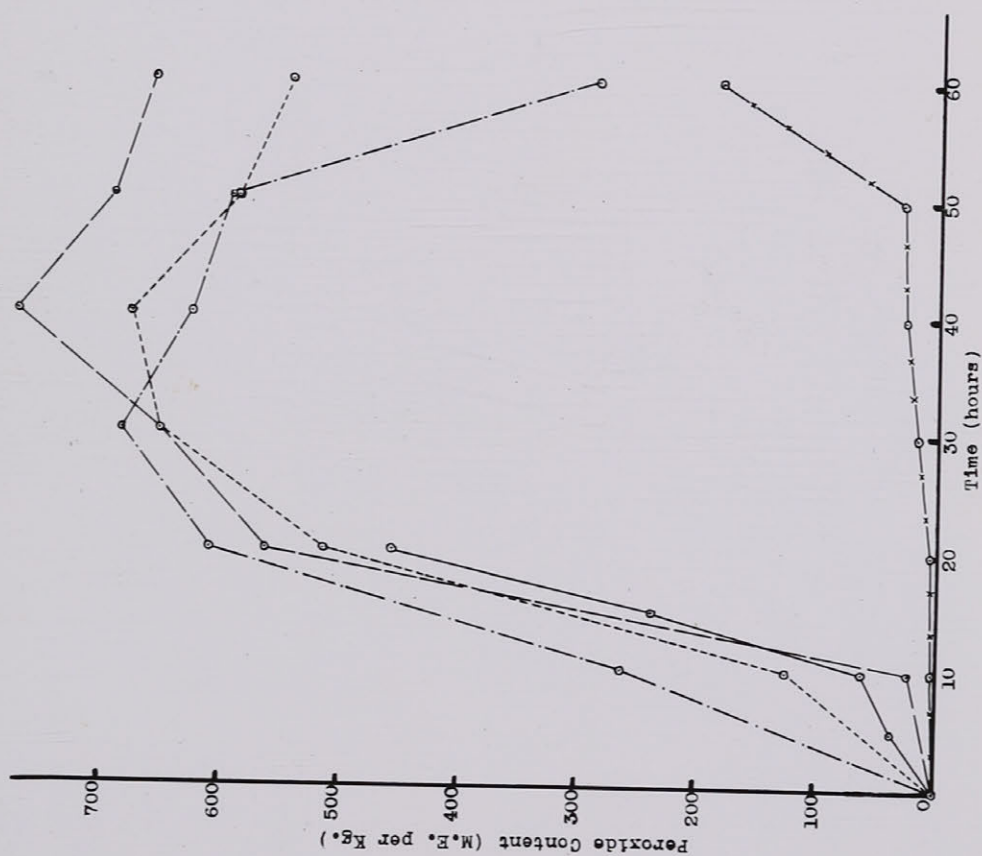
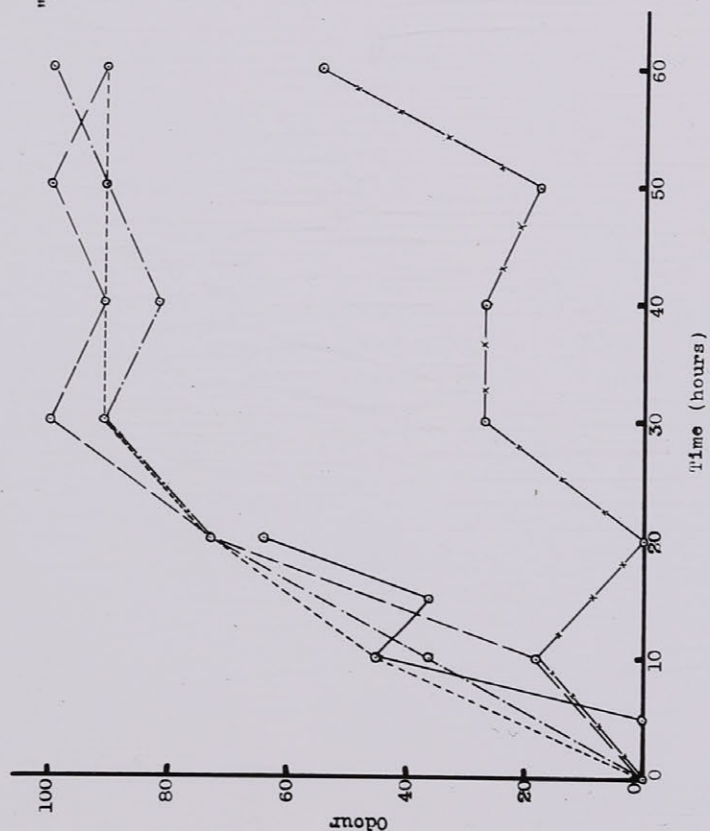


Figure 23
"FORMULA C" IN PROCESSING
Sample 1
2
3
4
5

Figure 24
"FORMULA C" IN PROCESSING



The results of the test on development of peroxides and reversion odour are shown graphically in Figures 25 and 26. A marked effect of Formula C in retarding reversion as well as peroxide formation is again shown. At the 0.01 per cent level formula C is much less effective than at the 0.1 per cent level.

c. Glycerol gallate (with addenda)

An alkali-refined linseed oil shortening of iodine number 65 was prepared and divided into five portions. One of these was kept as a control and to the other four, antioxidant mixtures were added as shown in Table XI.

TABLE XI

Glycerol Gallate (With Addenda)

Sample number	Percentage of each substance added				
	1	2	3	4	5
Antioxidants added:					
Glycerol gallate		.110	.530	.110	.550
Gallic acid		.006	.030	.003	.015
Citric acid		.003	.015	.003	.015
Vitamin E		.003	.015	.006	.030
Total	0.0	.122	.590	.122	.610

The results of the test on the development of peroxides and reversion odour are shown graphically in Figures 27 and 28.

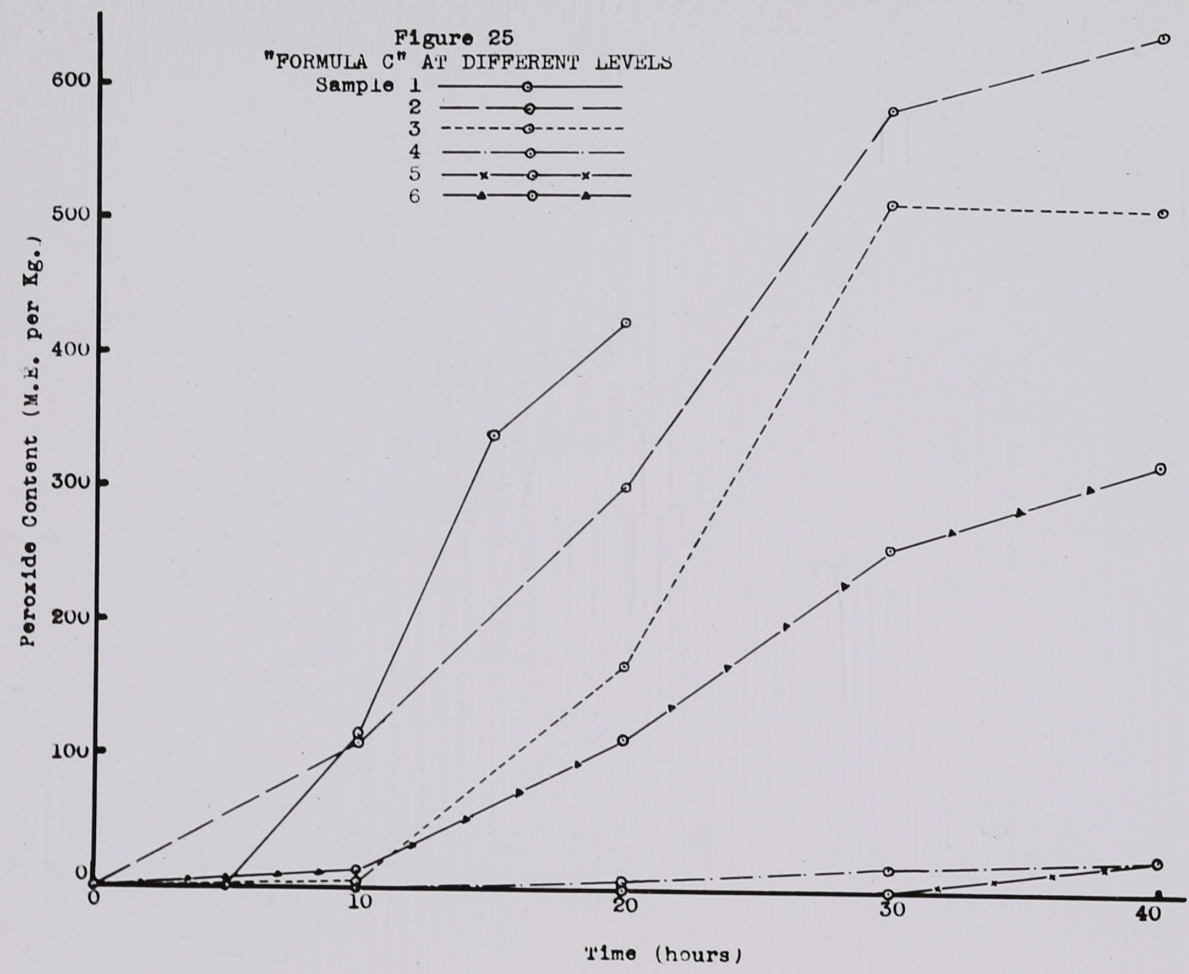
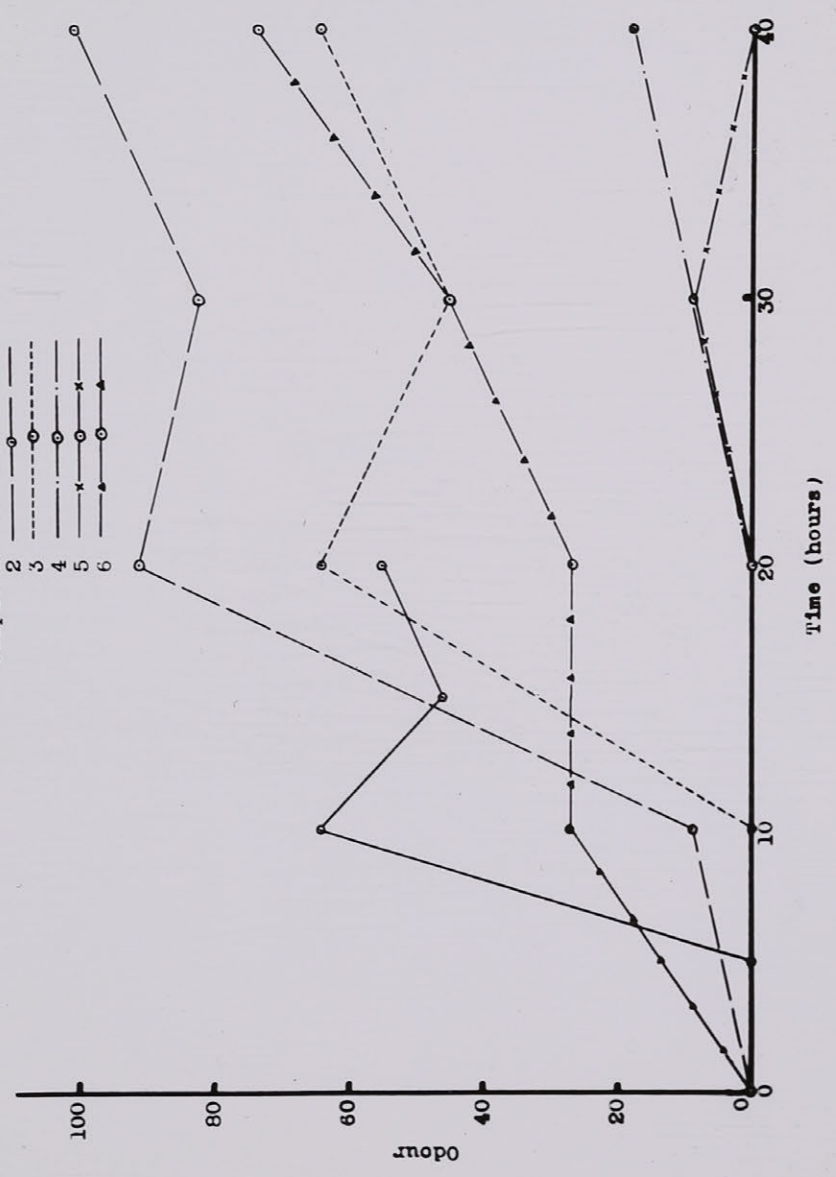
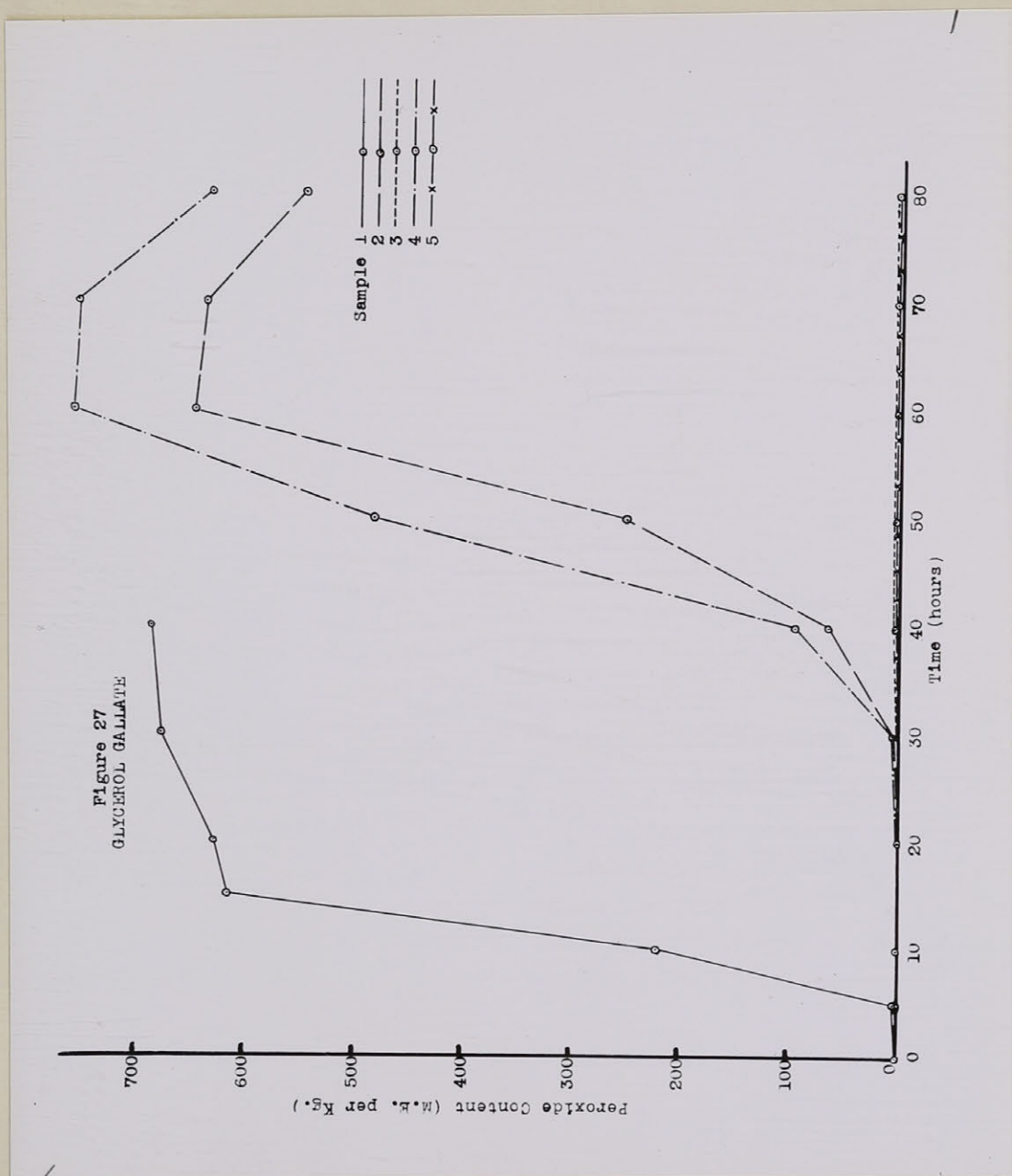
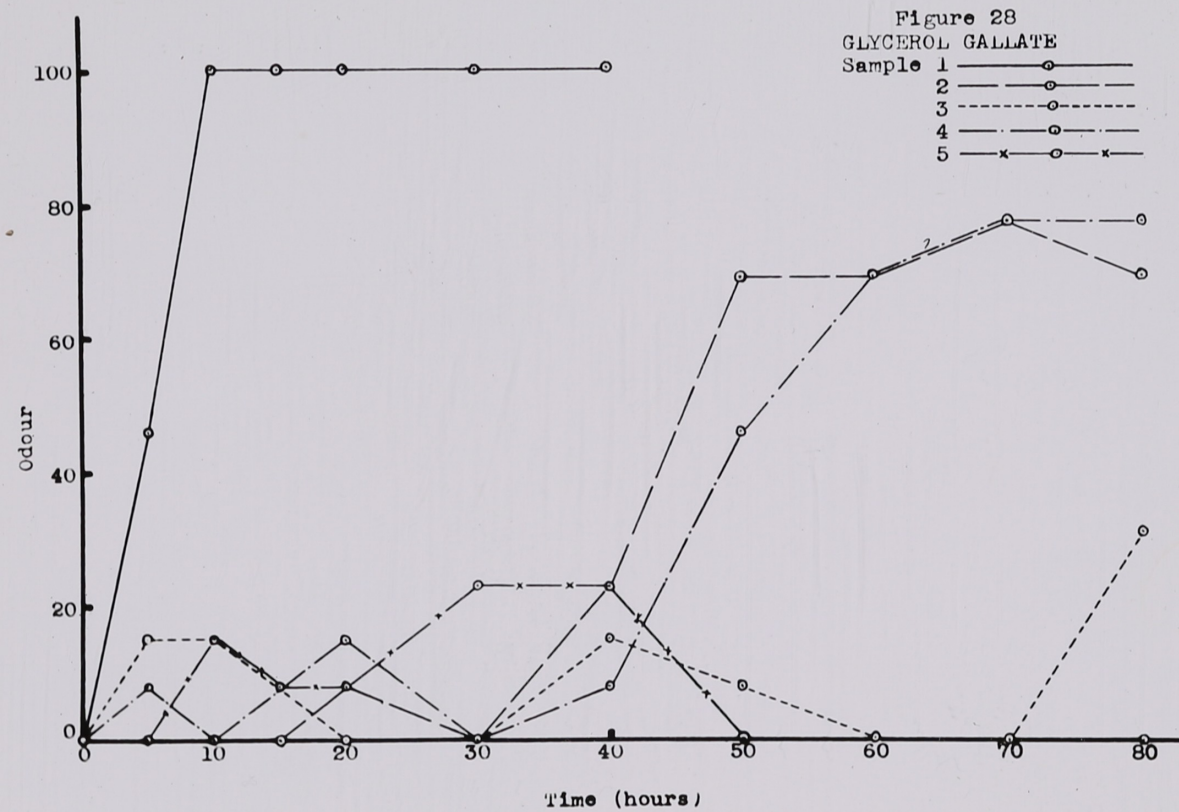


Figure 26
"FORMULA C" AT DIFFERENT LEVELS
Sample 1
2
3
4
5
6







This test was planned to study samples heated up to forty hours at 100°C., so these samples were given continuous heating. But as it was then seen necessary to continue the heating period since all samples with antioxidants were still relatively unchanged, the samples which had been heated for 10, 20, 30 and 40 hours were returned to the oven for a further forty hours of continuous heating, to become samples which had been heated from fifty to eighty hours.

The results here show antioxidants exerting an even greater stabilizing effect both toward peroxide formation and toward development of odour than had previously been observed. Although the control sample had changed greatly in ten hours, samples 2 and 4 had not changed much in forty hours and the samples 3 and 5 were still almost unchanged at eighty hours.

It seems indicated that these antioxidants may be somewhat more effective than Formula C as shown in previous tests, however the best results were with much higher levels of antioxidant than were studied with Formula C.

Following the observed effect of antioxidants to retard the development of the reversion odour, two experiments were set up to study their effect during baking.

d. Formula C with isopropyl gallate

An antioxidant was prepared which was seventy-five per cent Formula C and twenty-five per cent isopropyl gallate. It was added to four different shortenings prepared as described in Table XII at the level of 0.1 per cent. The four

shortenings thus treated and a control for each were tested for reversion in pastry and the samples were judged by a panel of 23 judges (Section A of the third year Household Science Class and a group of the post-graduate students in Agricultural Chemistry). Two girls prepared all the samples of pastry taking great care to have as near absolute uniformity as possible and three samples of pastry were prepared for judging from each sample of shortening so that 3×23 , or 69 judgments were obtained on the quality of each of the shortenings. The results were expressed as the percentage of the judgments on each sample of pastry which considered it satisfactory and these percentages were averaged for each three pastries to give a score for each shortening. The results are also shown in Table XII.

These were generally good samples of linseed oil shortening and the pastries from them were not generally considered unsatisfactory. The contribution of the antioxidant seemed negligible. Although in two of the three linseed oil shortenings tested the sample with the antioxidant received the higher score, the difference was very slight. It seems difficult to account for the great difference in scoring of the pastries from the two samples of Domestic Shortening. The author did not consider that these scores reflected a real difference.

After the judging was completed five of the judges and the author checked carefully the linseed oil samples to see if any of them could be considered to be free of the reverted

TABLE XII

Formula C with Isopropyl Gallate

Shortening Number	Composition of Shortenings					Score on ea. pastry sample	Score for each Shortening (average)
	% A	% B	% C	% D	% E		
1	100				-	45 46 100	64
2	100				0.1	79.5 95 100	91.5
3		100			-	18 69 75	54
4		100			0.1	11.5 29 94.5	45
5	50	50			-	34 54.2 94.8	61
6	50	50			0.1	48.4 59 84.6	64
7			80	20	-	34 70 70	58
8			80	20	0.1	39 64.5 79.5	61

A: Domestic Shortening

B: Linseed oil shortening of iodine number 82

C: Linseed oil shortening of iodine number 65

D: Alkali-refined sunflower seed oil

E: Antioxidant

flavour. It was agreed by all of us that this flavour was present in every one.

e. Isopropyl gallate with citric acid

An antioxidant was prepared from isopropyl gallate and citric acid in equal amounts. This was added to two portions of a linseed oil shortening (iodine number 68) at the levels 0.5 and 1.0 per cent. Pastries were prepared from a control portion of the same shortening and from each of these shortenings with antioxidants.

The pastry prepared from the shortening with 0.5 per cent antioxidant seemed to have slightly less reverted flavour than the control. It was however not free of this flavour. In the other sample of pastry a reverted taste could not be detected but there was a sharp taste of a different nature which was considered due to the antioxidant itself. This was so strong that it would have masked the reverted flavour.

V. DISCUSSION OF RESULTS

A. THE HYDROGENATION REACTION

1. The Catalyst

Reduction of the catalyst at temperatures of 400 to 450°C. as recommended by Hilditch (53) was found to give a less active product than if reduction was carried out at a temperature of about 500°C. This is in agreement with the work of Bennett (17) where the activity of the catalyst was found to increase with increased reduction temperatures up to 535°C.

Storing the catalyst in an atmosphere of carbon dioxide or of nitrogen did not preserve its activity since some catalysts stored in this manner had to be discarded within a week after their preparation. Catalysts stored in a fat seemed to have lost none of their activity after one month.

2. The Reaction Rate

Examination of the curves which show concentration of reacting substance (expressed as iodine number) plotted against time, and those which show the logarithm of the concentration plotted against time, suggests that the whole course of the reaction cannot be said either to be definitely zero order nor entirely first order. This finding can apply only to the apparatus used in these experiments and for the conditions of agitation which were employed. These may be important factors as suggested by Bennett (17). However, this seems the result that might be expected when dealing

with such a complex material (75, 86). If pure linoleic acid were hydrogenated the rate would be the resultant of two reactions -- linoleic to oleic, and oleic to stearic. Even though both reactions were monomolecular the resultant might not be. In these studies the relatively large amount of linolenic acid added to the complexity.

The effect of catalyst concentration on the rate of the reaction is shown clearly in Figure 8. Increasing the concentration from 0.3 to 0.5 per cent nickel more than doubled the amount of hydrogen absorbed by an alkali-refined linseed oil in thirty minutes. For an unrefined linseed oil, increasing the catalyst concentration from 0.4 to 1.0 per cent brought a four-fold increase in the amount of hydrogen absorbed in this time. These curves also show that there was a maximum effective concentration of catalyst for each oil under fixed conditions of hydrogenation.

The effect of impurities in the unrefined oil was to greatly retard hydrogenation as is also indicated in Figure 8. An unrefined linseed oil required about double the concentration of catalyst to bring hydrogenation to the same rate as in the refined oil. For the same amount of catalyst in each, the refined oil absorbed hydrogen two to three times as rapidly as the crude oil. It is interesting that both crude and refined oils seemed to have the same maximum hydrogenation rate when a sufficient amount of catalyst was present for each. This maximum rate would possibly be altered if other conditions, e.g., rate of agitation or mixing were altered.

The effect of temperature on the rate of the hydrogenation is shown in Figure 11. Increases within the range 80 to 150°C. produced marked increases in rate. Over the limits of this range the volume of hydrogen absorbed in 30 min. was increased about twenty-four times. Increases of temperature in the range 150 to 180°C. and probably for a short distance beyond were indicated to be much less effective in increasing the rate of hydrogenation.

The hydrogenation of fatty acids alone was shown to be quite a different problem from the hydrogenation of the glycerides (Figure 16). The results indicated that the free carboxyl groups had a marked effect in decreasing the activity of the catalyst and thus retarding the reaction. The rate during the first ten minutes was comparable to that observed in hydrogenating an alkali refined oil but beyond this time it fell off markedly. This seems due entirely to free carboxyl groups becoming fixed to the active nickel particles which hence-forth had no activity. Supplying fresh nickel catalyst started the reaction off again with the full initial rate, but again the carboxyl groups gradually reduced the number of active nickel particles so that the reaction almost stopped.

3. Conjugated Hydrogenation

It was interesting to observe the ease with which this newer type of hydrogenation could be carried out. Opportunities would not readily permit the comparison of the conjugated

hydrogenation of linseed oil at higher pressures with this method at atmospheric pressure, however, the work reported at higher pressures for other oils, e.g., sunflower seed oil, cottonseed oil, and by Rush (103) for linseed oil, has all shown the reaction to terminate at a minimum iodine number. Rush reports that this minimum point of reduction comes when practically all of the fatty acids have been converted to oleic, except in the case of linseed oil (where there was more unsaturation left).

The experiments carried out in this study also indicated that the reaction terminated at a minimum iodine number. It seems probable that the reaction at atmospheric pressure follows the same course as at higher pressures with the principal difference being in the time that is required.

4. Hardening by Isomerization

In the experiment conducted to bring about isomerization or elaidinization of the partially hydrogenated linseed oils, only small changes were observed. It is possible that a large proportion of iso-acids were already present and it is probable that the isomerization reactions reach an equilibrium so that a complete conversion does not occur.

5. Recovery of Catalyst

The experiments carried out indicated that to recover properly the catalyst it was not sufficient simply to remove the fat and fat-soluble substances which adhered to the catalyst, nor yet was it sufficient to submit the spent catalyst to

oxidation at temperatures of 600 and 700°C. followed by reduction in hydrogen. It is suggested that for activity comparable with that of a fresh catalyst it would be necessary to dissolve the nickel in acid, purify the solution and precipitate it again as in the original preparation.

B. FLAVOUR REVERSION STUDIES

1. Judgment of Quality

A quantitative estimate of quality seems basically to depend on organoleptic judgments by a panel of judges. We can agree with Trout, et. al. (110), from our own personal experience that a considerable mental effort is required of a judge. In the case of milk powders this was required by the transitory nature of the sensation. In these judgments it is the persistent nature of previous sensations which makes difficult the detection of the similar sensation in future samples, and which suggests its presence from samples actually not themselves creating it. In an attempt to stimulate the judges to do their best they were shown the judgments of the whole panel after each series had been judged and were encouraged to check any judgments which disagreed with the general opinion. This seemed the best incentive that could be given.

Two means seem available to increase the precision of the measurements of quality: first, a more or less lengthy period of training for the panel of judges; second, the requirement of a demonstration of high judging ability from each member of the panel. In these studies time did not

permit an extensive training period, and the number of persons available as judges would scarcely allow for any elimination.

In flavour judgments a considerable difference in quality was evident between duplicates. Even with most careful control in the manual operations of mixing, rolling, etc., these differences could not be avoided. If these operations could be completed mechanically, greater uniformity might be obtained. This might be possible if all shortenings were of the same hardness.

2. Modifications in Processing

Higher concentrations of catalyst seemed to produce a product of somewhat better quality. This was most noticeable with the unrefined linseed oil and may not have been due to the nickel itself as much as to the adsorbent powers of the carrier effecting a certain amount of refining. In the refined oil where the effect of the nickel concentration alone would show most clearly very little change was observed.

From the studies on hydrogenation at different temperatures it would seem that this factor has very little effect on the quality of the product. Temperatures of 150 to 180°C. would seem preferable only because they cause the reaction to proceed more rapidly.

Refining the oil did seem a means of improving the quality of the shortening in a number of the experiments. In addition to those experiments designed to study this effect, may be added the evidence obtained in the experiment with various proportions of catalyst used in hydrogenation. In

those experiments that did not show any advantage for increased refining, the variability of judgments included in "error" was so great that no conclusions were possible from the data. In no case was contradictory evidence obtained.

The effect of the degree of hardening within the range of iodine numbers 60 - 90, seems not great. When the refining technique was the same for all samples compared a slight superiority was found for those products with an iodine number below 70. However in the later tests where the samples with the higher iodine numbers had also received additional refining any disadvantage they may have had was either compensated for or overshadowed by the advantage of the refining.

In the experiments on blending sunflower seed oil with the harder samples of linseed oil shortening only mixtures containing 65 to 80 per cent of the latter were studied. It was not found with any of the shortenings used that the characteristic flavour could be masked when its proportion was so high. The use of larger proportions of partially hardened sunflower seed oil with small amounts of linseed oil shortenings might give a product in which it would be very difficult or impossible to detect the reverted flavour, but this did not seem a satisfactory solution to the problem.

Different samples of hot-pressed linseed oil do not differ appreciably; neither do samples of cold-pressed oil differ from one to another; nor do hot-pressed oils in general show any differences from cold-pressed oils in respect to the quality of

shortening produced from them.

3. Causes of Reversion

It has been shown, first, that a component of the saponifiable fraction of linseed oil is responsible for flavour reversion, and further, that this is probably linolenic acid. To give the reverted flavour it is not necessary for this component to exist as a free fatty acid, but it does seem necessary that it be subjected to the conditions of hydrogenation. Thus the origin of the odour indirectly would seem to be linolenic acid, but more directly to be some product of it formed during hydrogenation. Regarding the nature of this product it can only be said that it does not seem to be offensive in itself, but on heating it produces the substances which are directly responsible for the reverted flavour and odour. These latter substances may be removed by deodorization whereas the basic cause may not; it remains and is able, on subsequent heating to form again these more volatile offenders. In the work here completed the identification of this substance has not been attempted. There are many possibilities some of which may be eliminated. The ordinary oleic, linoleic and linolenic acids are ruled out; likewise the usually occurring iso-acids cannot be responsible.

If linolenic acid were first hydrogenated at the Δ^{15-16} double bond the ordinary linoleic acid would be obtained and no reversion should occur thereafter. Therefore all of the linolenic acid cannot undergo this change before some other

takes place. The other change may be either reduction at one of the other double bonds or an isomerization reaction. Either of these changes may be followed by the other. The isomerization may be such as to cause migration of double bonds and it may also involve cis-trans changes. The possibilities thus created are many and the available methods of study may not be adequate to give a definite answer.

Regarding the reversion problem it would seem indicated that refining cannot offer a complete solution. Some possible answers may however be suggested. The complete removal of linolenic acid (if this could be accomplished) should bring complete freedom from reversion, but such a plan is quite impractical. There is a possibility of hydrogenating conditions being made so highly selective that all linolenic acid would be changed to ordinary linoleic acid before any other change occurred. Also some changes, e.g., oxidation, might be made to occur in the original linolenic acid so that on hydrogenation the reaction would take a more favorable course. Then there are certain possibilities of changing the product formed in the hydrogenation. A subsequent isomerization might restore the structure to one which is heat-stable and inoffensive. Prolonged heating (and possibly oxidation) followed by deodorization might convert the basic substance into volatile products which could be removed. Finally certain substances might act as inhibitors to the decomposition on heating.

The experiments described above have investigated these

suggested solutions. Oxidation of the oil prior to hydrogenation was found to bring about changes in the flavour of the product but they could not be considered favourable. The radically different technique of conjugated hydrogenation was found not sufficiently selective. Also the highest temperatures and catalyst concentrations which were used and with the relatively low pressures used in all the hydrogenations with the regular technique, failed to produce conditions of sufficient selectivity. It seems likely that conditions of such high selectivity as would be required might be very difficult to find.

Isomerization reactions to restore the reverting substance into a heat-stable form were not brought about by heat alone or by heat with sulphur dioxide or selenium. The complete conversion of the reverting substance into volatile products did not occur under the conditions employed in the experiments described. The experiments relating reversion to oxidation and the use of antioxidants to retard this change seemed promising. The development of a reversion odour and the rapid formation of peroxides occurred in close succession. Certain antioxidants were able to retard greatly the development of this odour. However using antioxidants even at very high levels did not prevent the development of a reverted flavour during baking tests.

VI SUMMARY

The hydrogenation of crude and refined linseed oil has been studied in a shaker-agitated bottle employing different concentrations of nickel catalyst and different temperatures.

The catalyst was prepared by the dry reduction of nickel carbonate on silica gel. For maximum activity it was reduced at 500°C. and stored in a fat. The activity of a spent catalyst was not completely restored by washing with a fat solvent, oxidizing in a furnace and reducing again in hydrogen. The solution in acid, purification and reprecipitation as nickel carbonate seemed necessary.

Because of the complexity of the system and possibly inadequate mixing, the reaction did not proceed exactly as either a zero order or a first order reaction.

Increases of catalyst concentration up to a definite level effected large increases in reaction rate. This was observed with both crude and refined linseed oil, but the actual concentration of catalyst required by the crude oil for any given rate was approximately double that required by the alkali refined oil. With sufficient catalyst the maximum reaction rate was the same for both crude and refined oil.

An increase in temperature within the range 80 to 150°C. also brought a large increase in reaction rate. Below 80°C. and above 150°C. the rate of the reaction changed very little with variation of temperature.

The free fat acids of linseed oil hydrogenated alone were

found to deactivate the catalyst. Conjugated hydrogenation of linseed oil with alcohol was accomplished at approximately atmospheric pressure but the reaction stopped when the product had an iodine number of 100.

The phenomenon of reversion in linseed oil shortenings has been studied. It was found that this flavour and odour are characteristic of the hydrogenated product. Although linseed oil on heating produces a variety of "off" odours, none of them resemble this reverted odour. Linolenic acid has been indicated as the component of the oil which is responsible for this phenomenon. The effect is produced without regard to the content of free fatty acids, but it does seem that hydrogenation is an essential factor. Thus it has been postulated that the basic cause of reversion is some product of linolenic acid which is formed during hydrogenation. This substance probably has a large molecule but on heating it decomposes more or less rapidly to form the volatile products which are directly responsible for the reverted flavour and odour.

Possible means of preparing a linseed oil shortening which would be free from reversion have been investigated. First, attempts have been made to find conditions of hydrogenation, or treatments of the oil which would prevent the formation of that product which is responsible. Secondly, attempts have been made to change this product after its formation into a heat-stable form, to decompose it completely and so remove it from the fat, or finally to prevent its normal decomposition on heating by the use of substances which inhibit this change.

VII AUTHOR'S CLAIM OF ORIGINAL WORK
AND CONTRIBUTION TO KNOWLEDGE

In the published literature no study of flavour reversion in linseed oil shortening was found.

A number of workers have reported on the hydrogenation of linseed oil where the interest lay in studying the course of the reaction. Nevertheless, it was necessary for the author to work out for himself the means of control and regulation, and to study the effect of the various factors on the reaction as carried out in this study. Conjugated hydrogenation at atmospheric pressure has not to the author's knowledge been previously attempted.

The characteristic nature of flavour reversion in linseed oil shortening has not before been pointed out nor has it been distinguished from the development of a variety of "off" odours produced on heating the oil itself. The proof of reversion being associated with linolenic acid and the survey of the possibilities for producing a non-reverting linseed oil shortening are, to the author's knowledge, entirely original. Studies of reversion in different fractions of the shortening, of its relation to oxidation and the effect of antioxidants in retarding it are believed to be original contributions.

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